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AMERICAN

CHEMICAL JOURNAL

THE OSMOTIC PRESSURE AND FREEZING-POINTS OF SOLUTIONS OF CANE-SUGAR.[1]

BY H. N. MORSE AND J. C. W. FRAZER.

Nearly three years ago the authors published[2] under the title "The Preparation of Cells for the Measurement of High Osmotic Pressures" an account of the results which they had obtained with the electrolytically deposited copper ferrocyanide membrane, previously described[3] by Morse and Horn. Pressures of over 30 atmospheres had been obtained and it was supposed by the authors that, having solved in a satisfactory manner the problem of depositing the membranes and having overcome, in a measure, the difficulties connected with the assembling of the different parts of the cell, they could proceed, without further delay, to the measurement of osmotic pressure. But it soon appeared that a third problem, the most difficult of all, remained to be dealt with, *i. e.*, the problem of the *porous wall*. The porous cups in which the high pressures referred to had been obtained were a part of a lot of 100, which were made for the authors at a pottery in a neighboring city. Out of this number 25 or 30 had been found to answer the requirements moderately well and it was not doubted that others equally good, or better, could be readily procured. In this we were greatly mistaken, for among the nearly 500 cells which were subsequently made for us at various potteries *not one* was found suitable for the measurement of osmotic pressure. An entire year was spent in procuring and testing porous cells from different sources, but to very little purpose, except to convince us that the problem of producing the cells must be worked out in the laboratory rather than at the pottery. The potters, in attempting to produce, by their methods, porous vessels which they conceived to be suitable for our purposes, unwittingly introduced or magnified defects from which the earliest cells were fairly free. Our later experience has shown us that a different result was not to be expected, inasmuch as the production of the correct texture of porous wall for the measurement of osmotic pressure involves a resort to methods not ordinarily practiced by the potters.

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[1] This work has been carried on with the aid of grants from the Carnegie Institution.

[2] THIS JOURNAL, **28**, 1.

[3] *Ibid.*, **26**, 80.

Having failed to procure cells of the required character, we proceeded to make a microscopic study of thin sections of a considerable number of those which had been previously tested with membranes, selecting for the purpose cells which could be classified as fairly good, bad and indifferent. It was hoped, by this means, to discover the peculiarities of texture which determine the suitability of a porous wall for experimental work and, having found them, that methods might be devised which would insure the reproduction, at will, of the essential qualities. The work along these lines is far from finished and the results are, therefore, not ready for publication. We have already succeeded, however, in producing, in the laboratory, a few cells of almost ideal excellence and with these the measurements of pressure here recorded were made.

In order to provide others, as well as ourselves, with a safe basis for a criticism of the procedure and for a judgment of the weight to be assigned to the results, also to avoid unnecessary repetition in future communications, we shall describe, in some detail, the apparatus which has been employed and the methods which have been followed, beginning with the manometer.

The form of the manometers which have been used in these experiments is shown in Figs. I. and II. Two such instruments have been employed, which will be designated as No. 3 or No. 4 whenever there is occasion for mentioning one or the other specifically.

Originally, *i. e.*, after the first filling, No. 3 had a length of air column amounting to about 413 mm. under atmospheric pressure, at ordinary temperatures, while the length of air column in No. 4, under similar conditions, amounted to about 428 mm. But, since it is necessary from time to time to open and refill the instruments, the quantity of the enclosed air is subject to some variations. The diameter of the bore is about 0.5 mm. Greater accuracy of measurement could, of course, be secured by using longer manometers with larger volumes of enclosed air, but development in this direction is limited in various ways. It is rarely possible to find tubes, of any great length, which are sufficiently straight throughout for use as manometers. Again, an objection to long manometers is the greater difficulty which is experienced with them in avoiding accidents while securing them in their places in the cells. The manipulation at this point is difficult, even under the most favorable conditions. But the principal consideration which renders the use of large volumes of air inadvisable is the obvious fact that the contraction, under pressure, of the gas in the manometer is attended by an equivalent increase in the volume of the contents of the cell. The absolute volume of this contraction should not, of course, be so great as to result in a sensible dilution of the solution.

The air column, under high pressures, is very short, amounting, in the manometers used by us, to only about 16 or 17 mm. when the pressures to be measured reach 25 atmospheres. The accurate calibration of the instruments is, therefore, a matter of great importance. The method of calibration which we have used is similar, in principle, to that which is employed for eudiometers. Fig. II. represents the instrument which we constructed for the purpose.

A steel screw, with a light, rather long, wooden handle at its lower end *a*, serves to adjust the short thread of mercury at *h*, in any desired position in the manometer tube, the thread being separated from the mercury below by a short column of air ; *b* is a cup of hard rubber, which is turned to the proper form on the lathe, bored and threaded for the screw *a*. In cutting the thread upon the screw great pains are taken to secure an exact fit to the thread in the cup, in order to avoid leakage of mercury. The glass tube *i* is fixed in the rubber cup by means of litharge-glycerine cement, which is shown at *d*. The tube is enlarged at *c* to prevent slipping and contracted at *e* in order to hold the rubber stopper *f* more firmly in its place. A still further provision against leakage of mercury is made by slightly oiling the upper end of the screw and allowing cement to solidify about the thread. Finally, the whole thread is lubricated with a rather stiff paste, made by fusing together rubber, vaseline and paraffin.

The manometer has etched upon it three lines of reference, two of which, *g*, are located in the same horizontal plane—one below the bulb and the other opposite to it on the ascending limb. The third line, which is not shown in the figure, is located near the top of the manometer. The instrument should not be otherwise graduated, owing to the interference of lines with readings by the telescope.

Near the open end of the manometer the tube is enlarged to a bulb, as shown at *j* in Fig. I. This feature of the instrument is indispensable, since without it, it is impossible to keep the manometer in the cell when more than very moderate pressures are developed. Formerly we employed, in its place, a cone-shaped mass of shellac, which was attached to the glass, but this, though it rendered good service for a time, was liable, after a few experiments, to become detached in consequence of the penetration of liquid between the glass and the shellac.

The bulb in the descending limb of the manometer, which serves as a reservoir for the mercury, is made as large as is consistent with the required strength of the wall. The purpose of this is two-fold : first, the solution is much less likely

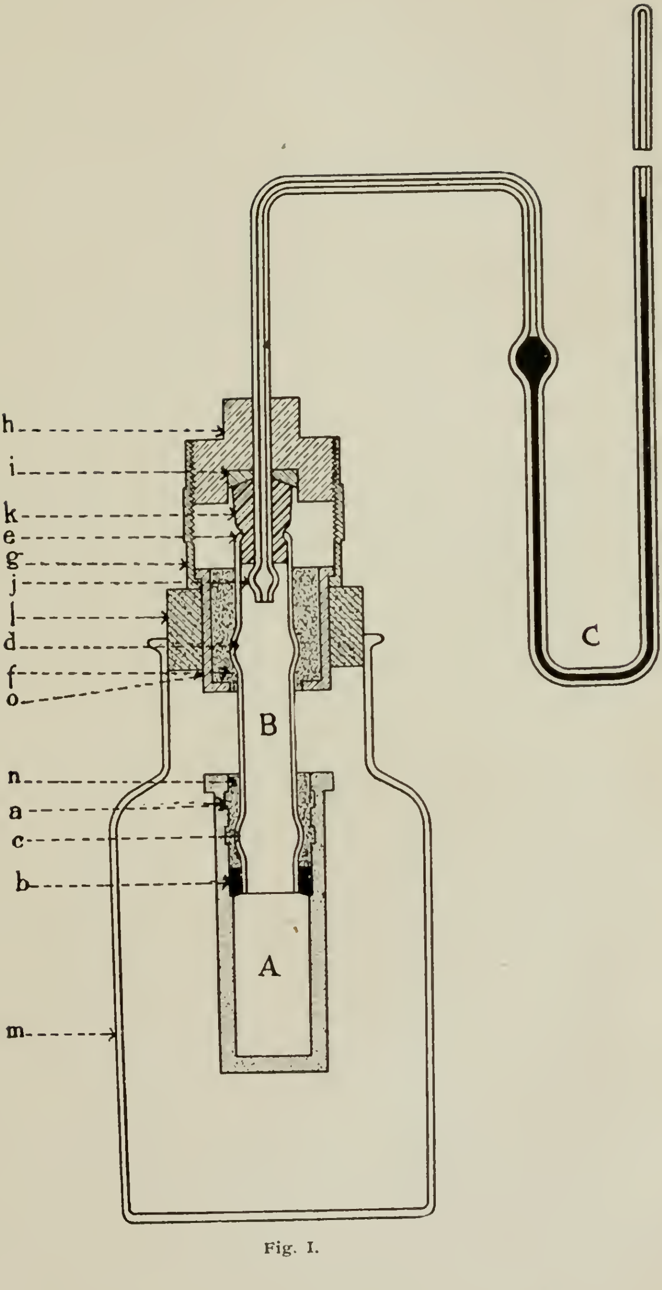

Fig. I.

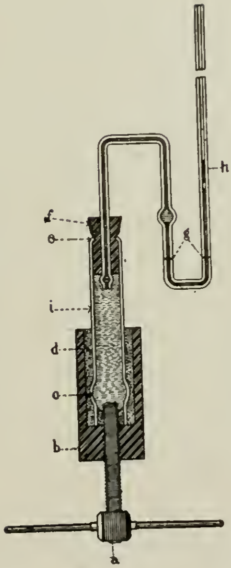

Fig. II.

to get past the mercury into the air space during the somewhat strenuous manipulation which is necessary when the manometer is inserted in the cell ; and second, the level of the mercury in the bulb (which must be known when a reading is made) is subject to such slight variations in a large bulb that one determination of its height above the line of reference serves for all the readings which are made during any single experiment. An ample reservoir for the mercury is quite essential, since the whole apparatus, when in use, is buried in hair to insure an even temperature of the contents of the cell.

The most trying and critical operation connected with the setting up of a cell is the insertion of the stopper carrying the manometer. The pressure which must be brought upon the stopper to force it into its place is considerable, and this cannot be relaxed, even in a slight degree, from the beginning to the end without danger that a portion of the enclosed air will pass the bend in the tube and escape into the bulb. This difficulty can be remedied in great part, and will be hereafter, by blowing another bulb near the bottom of the ascending limb of the manometer.

Before proceeding to describe the method of calibrating the manometer, it may not be superfluous to explain that all observations are made with a telescope, which is provided with a micrometer eye-piece and that all readings are taken from a standard meter, which is mounted in a vertical position at a short distance from the cathetometer. The meter scale and the cathetometer rest upon foundations which do not come in contact, at any point, either with the floors or walls of the laboratory and the stability of the instruments, which is thus secured, is entirely satisfactory. The cells, while under observation, and the manometer while undergoing calibration, rest upon the same foundation as the meter scale. Great care is taken to secure an exactly vertical position for the cathetometer, the standard scale and the manometer. The first is adjusted until the vertical spider line of the telescope will follow thin plumb-lines in planes at right angles to one another, while the correct positions for the other two are found with the aid of the telescope and plumb-lines.

The calibration of the manometer is carried out in the following manner: The tube *i* is filled with mercury and the manometer (with its upper end still open) is fixed in its place as shown in Fig. II. The method of introducing the stopper *f* into the tube *i*, when the latter is full of liquid, will be explained later, in connection with the manipulation of the cell. Having brought the apparatus to a vertical position with the aid of adjustable clamps attached to a stiff steel standard, which is firmly fixed in the foundation, the screw is turned upwards until the mercury fills the manometer to within about 1 mm. of the top. A drop of mercury is then placed upon the upper open end of the tube and the screw turned in the other direction. A short thread of mercury (*h*, Fig. II.) is thus introduced, which is separated from the unbroken column below by a shorter column of air. The thread of mercury is made to descend in the tube until its lower end is exactly opposite the line of reference. The distance between its two ends is then determined with the aid of the telescope and the standard scale.

Having found the length of the space filled by the fixed column of mercury just above the line of reference, the thread is pushed upwards until its lower end occupies exactly the previous position of the upper end, when another set of readings is made. In this way the thread is placed end to end and the length of the space occupied after each setting is determined until the top of the tube is reached.

In order to use conveniently the data thus obtained all the observations are reduced to a calibration unit and the results are plotted in the form of a curve. The calibration data for the instruments Nos. 3 and 4, which were the ones used in these experiments, are given in the following tables. The first column in each table gives the actual readings on the graduated scale. The second column gives the differences between the successive readings, *i. e.*, the length of the mercury thread in the different parts of the tube. The readings on the meter, which would have been obtained if the zero of the graduated scale had coincided with that of the manometer, are given in the third column.

Table I.—Data for Calibration of Manometer No. 3.

I. Readings upward on scale.	II. Differences.	III. Readings on meter calculated from the zero-point.	IV. Products of number of settings by mean space filled.	V. Correction values.
918.77	13.92	13.92	13.858	—0.06
904.85	14.08	28.00	27.716	—0.28
890.77	14.06	42.06	41.574	—0.49
876.71	14.08	56.14	55.432	—0.71
862.63	14.13	70.27	69.290	—0.98
848.50	14.12	84.39	83.148	—1.24
834.38	14.07	98.46	97.006	—1.45
820.31	14.07	112.53	110.864	—1.67
806.24	14.11	126.64	124.722	—1.92
792.13	14.02	140.66	138.58	—2.08
778.11	14.03	154.69	152.438	—2.25
764.08	13.96	168.65	166.296	—2.35
750.12	13.92	182.57	180.154	—2.42
736.20	13.81	196.38	194.012	—2.37
722.39	13.75	210.13	207.870	—2.26
708.64	13.68	223.81	221.728	—2.08
794.96	13.71	237.52	235.586	—1.93
681.25	13.63	251.15	249.444	—1.71
667.62	13.65	264.80	263.302	—1.50
653.97	13.67	278.47	277.160	—1.31
640.30	13.63	292.10	291.018	—1.08
626.67	13.73	305.83	304.876	—0.95
612.94	13.75	319.58	318.734	—0.85
599.19	13.75	333.33	332.592	—0.74
585.44	13.71	347.04	346.450	—0.59
571.73	13.75	360.70	360.308	—0.39
557.98	13.81	374.60	374.166	—0.43
544.17	13.76	388.36	388.024	—0.34
530.41	13.78	402.14	401.882	—0.26
516.63	13.77	415.91	415.740	—0.17
502.86	13.76	429.67	429.598	—0.07
489.10	13.89	443.56	443.456	—0.10
475.21	13.75	457.31	457.314	+0.004
461.46				

Table II.—Data for Calibration of Manometer No. 4.

I. Readings upward on scale.	II. Differences.	III. Readings on meter calculated from the zero-point.	IV. Product of number of settings by mean space filled.	V. Correction values.
901.69	12.55	12.55	12.186	—0.364
889.14	12.42	24.97	24.372	—0.598
876.72	12.45	37.42	36.558	—0.862
864.27	12.50	49.92	48.744	—1.176
851.77	12.34	62.26	60.930	—1.330
839.43	12.52	74.78	73.116	—1.664
826.91	12.34	87.12	85.302	—1.818
814.57	12.51	99.63	97.488	—2.142
802.06	12.40	112.03	109.674	—2.356
879.66	12.41	124.44	121.860	—2.580
777.25	12.42	136.86	134.046	—2.814
764.83	12.32	149.18	146.232	—2.948
752.51	12.45	161.63	158.418	—3.212
740.06	12.38	174.01	170.604	—3.406
727.68	12.38	186.39	182.790	—3.600
715.30	12.30	198.69	194.976	—3.714
703.00	12.34	211.03	207.162	—3.868
690.66	12.33	223.36	219.348	—4.012
678.33	12.43	235.79	231.534	—4.256
665.90	12.35	248.14	243.720	—4.420
653.55	12.28	260.42	255.906	—4.514
641.27	12.27	272.69	268.092	—4.598
629.00	12.14	284.83	280.278	—4.552
616.86	12.16	296.99	292.464	—4.526
604.70	12.14	309.13	304.650	—4.480
592.56	12.01	321.14	316.836	—4.304
580.55	12.00	333.14	329.022	—4.018
568.55	12.05	345.19	341.208	—3.982
556.50	11.92	357.11	353.394	—3.716
544.58	11.88	368.99	365.580	—3.410
532.70	11.90	380.89	377.766	—3.124
520.80	11.80	392.69	389.952	—3.738
509.00	11.85	404.54	402.138	—2.402
497.15	11.79	416.33	414.324	—2.006
485.36	11.65	427.98	426.510	—1.470
473.71	11.71	439.69	438.696	—0.994
462.00	11.70	451.39	450.882	—0.508
450.30	11.66	463.05	463.068	+0.018
438.64				

Referring to Table I., containing the calibration data for manometer No. 3, it will be observed that in setting the mercury thread 33 times, end to end, a space was covered which, measured on the standard scale, amounted to 457.31 mm. Dividing this number by 33, the number of settings, the average length of the space filled by the fixed amount of mercury is found to be 13.858 mm. The mercury thread was, therefore, regarded as containing 13.858 volume or calibration units. Column IV. gives the multiples of this number corresponding to the several readings in column III. The differences are contained in column V. They are, of course, the corrections which are to be applied at the 33 points in order to convert actual into calibrated or volume readings.

In the same way, the average space filled by the mercury thread was found to be 12.186 mm. in manometer No. 4 and the thread was, therefore, regarded as having a volume of 12.186 calibration units.

The corrections contained in column V. of each table were used as ordinates to plot curves, lines representing the manometers serving as the axes of abscissas.

The coöperation of two persons is necessary in a calibration experiment, one of whom sets the mercury thread while the other directs his movements and makes the readings from the telescope. In order to set the thread correctly, it is quite necessary to tap the tube vigorously and to continue doing so each time until no further movement of the mercury can be observed.

The method here described has the advantage that the calibration of a tube can be carried to any required degree of refinement, since by beginning at other points, above or below the reference line, any desired number of intermediate ordinates may be secured for the correction curve.

To fill a manometer, it is connected at the bottom, by means of a rubber tube, with a reservoir of mercury which can be raised or lowered according as the air is to be expelled from, or drawn into the instrument. At the top it is joined to an apparatus consisting of two connected tubes, one of them containing glass wool upon which has been deposited resublimed phosphorus pentoxide and the other solid potassium hydroxide and calcium chloride, to remove from the air, before it enters the pentoxide tube, carbon dioxide, ammonia and a portion of the water.

At intervals of half an hour, air thus purified is repeatedly drawn into and expelled from the manometer, which is finally closed in the following manner: A disk of sheet platinum is heated to a bright red color, near the center, with the tip of the blow-pipe flame. The heated spot, on the side opposite to the flame, is rubbed with a fragment of manometer tubing until a sufficient quantity of glass, in a thin fluid condition, has accumulated upon the metal. The manometer is then instantly closed by touching its upper end with the liquid glass. Afterwards the glass is rounded off by softening the extreme end of the manometer in the flame, while the air within is under slightly diminished pressure.

The open end of the filled manometer is immersed in mercury and there attached to the arrangement which is to serve as an adjustable reservoir in determining the volume of the enclosed air. This consists of a small rubber tube to which is joined a piece of manometer tubing, having the same bore as the manometer itself. Before connecting with the manometer, the rubber tube and a portion of the glass tube are filled with mercury, care being taken to insure the expulsion of all air from the former.

To determine the quantity of enclosed air, the manometer is fixed in a vertical position before the cathetometer, the level of the mercury in the reservoir tube is adjusted to that of the column within the manometer, pains being taken to ascertain that the relation of the two is not permanently altered by pinching the rubber connecting tube. Finally, the readings in millimeters are converted, with the aid of the calibration curve, into calibration volumes, which are afterwards reduced to their value under standard conditions of temperature and pressure.

When a manometer is closed in the manner here described, there is some doubt as to the volume which should be assigned to that portion of the bore the form of which is affected by the softening of the glass. Professor Abegg has kindly called our attention to one method of obviating this difficulty—that of displacing the air in the upper end of the manometer with a short column of mercury. The device is, no doubt, an excellent one, but we have been unable to employ it successfully in our manometers. In the few cases where we have tried it, we found that the separation of the necessary thread of mercury involved a roughness of manipulation which appeared to endanger the instrument. Moreover, we were unable to effect a sufficiently complete dislodgment of the air from the space which the mercury should fill.

The form of the interior surface of the tubes, in the region in question, is usually quite uniformly conical or spherical in appearance and we have assumed it to be strictly so in estimating the capacity of the upper ends of our manometers. Nevertheless, whenever it has been necessary to open a manometer for the purpose of refilling it, we have laid aside for further examination the end which was cut off.

After filling a manometer and finding the volume of the enclosed air, the exact distance between the two lines of reference on the vertical limb is ascertained and the capacity of the tube above the upper line is calculated, once for all. In the subsequent work, all readings are referred to one or the other of these lines and it is not necessary to locate, each time an observation is made, what the observer would regard as the proper starting-point at the top after correction for the change in the form of the bore.

The process of preparing the cell for use is so complex that we shall describe the different steps in their order, under the headings 1, 2, 3, etc.

1. The porous cell, designated by A in Fig. I., is mounted on the lathe in a chuck, the construction of which was explained in our earlier communication and, while slowly turning, it is ground internally to a distance from the end equal to somewhat more than a third of its length. The grinding is continued until the shoulder, formed at the bottom of the ground

area, extends entirely around the cell and is of sufficient width to afford an ample support, at all points, for the soapstone ring *b*. Afterwards two channels, one of which is designated in the figure by the letter *a*, are cut into the wall in order to prevent the dislodgment of the cement under pressure. The machine which was constructed for the grinding process is bolted to the tool carriage of the lathe. It carries a carborundum disk which makes about 9,000 revolutions per minute. At this speed the work is quickly accomplished without injury to the cell.

2. The glass tube B, which connects the cell A with the manometer C, should not be unnecessarily large or long. It is, at the best, the weakest part of the entire apparatus, *i. e.*, the part which is most likely to burst under high pressure. It should, therefore, be selected, if possible, from stock which has been thoroughly tested as to the toughness and the enduring qualities of the material. Otherwise one is liable, at a critical moment, to lose the labor of several weeks. The tube is enlarged at *c* and at *d*, where it is afterwards surrounded with cement. Both enlargements are indispensable, for without them the tube will either be pushed out of the cell or through the metal piece *o*. Furthermore, it is contracted at *e* to give a stronger grip upon the rubber stopper *k*.

3. The soapstone ring *b* plays an important rôle in the apparatus and it must be fitted to its place with great care. It is bored and turned on the lathe until it will slip over the end of the glass tube and into the cell. Its lower end is beveled inwards to prevent the lodgment of air.

To make a tight joint between the stone and the glass and to bind the two materials firmly together, the tube, with the ring in place, is inverted, and any space which is left between them is filled with molten shellac. The tube and ring are then placed in an air-bath, in the inverted position, and heated until the shellac is solid at a temperature a little above 100°. The reason for raising the fusing-point of the shellac by distilling out the more volatile matter will be understood when the next step is described.

4. The cement, which is employed to fix the glass tube B and the soapstone ring in their places in the cell, must be effectually protected from any contact either with the solution with which the apparatus is filled or with the water in which it is immersed. For this purpose the lower end of the glass tube, the soapstone ring and the whole of the ground surface within the cell are repeatedly painted with a rather dilute solution of rubber, which is prepared by first fusing pieces of black tubing and then dissolving the product in carbon bisulphide. The liquid is spread as uniformly as possible and, after each application, the wet surfaces are allowed to dry for a time. When a coating of sufficient thickness has been obtained, the soapstone ring, which is now firmly attached to the glass tube, is inserted in the cell and crowded into its place on the shoulder. The last operation is liable to lacerate, more or less, the rubber covering of the cell wall. To repair any damage of this kind and also to insure a tight joint between the clay wall and the soapstone ring, the whole cavity above the latter is again painted with the rubber solution. The apparatus is then placed in an air-bath and maintained at a temperature of 100° until the rubber becomes quite hard, but not brittle. Finally, the space between the cell wall and the glass tube is filled with the usual mixture of lead oxide and glycerine. It is to be noted, in this connection, that the oxide which is prepared in the laboratory, by heating the carbonate, gives much more satisfactory results than are obtained with the commercial litharge. When the cement has hardened—which it should be allowed to do for several days before the cell is used—its upper, exposed surface is also covered with rubber.

We have tried to substitute rings of hard rubber for those of soapstone, but without success. Every cell has cracked in which a ring of the former kind was used, apparently without any other cause than the diversity of the expansion coefficients of the materials.

5. The arrangement by which the stopper and manometer are held in the cell consists of the four brass pieces designated by the letters *o*, *g*, *h* and *i*. The piece *o* is firmly fixed in its place with litharge-glycerine cement, after the completion of

the preparations which have been described under 4. The width of *g*, under the flange, is equal to the greatest diameter of the cell. If, after burning, the width of the cell at the top is found to be somewhat greater than that of *g*, the rim of the former is ground to size while the cell is mounted on the lathe for the purpose of grinding out the interior.

The collar *g* is threaded internally about two-thirds its length from the top and is provided, at the lower end, with an interior flange which locks with the exterior flange of *o*. The surface of the raised, central portion of the outside is milled to provide a firmer hold for the hands.

The nut *h* is threaded externally to fit the interior thread of the collar *g*. At the upper end it is made hexagonal in form, in order that it may be held with a wrench while the stopper is driven into the cell by turning the collar *g*.

In order to obtain satisfactory measurements of osmotic pressure, it is indispensably necessary that all parts of the stopper *k*, which lie outside of the glass tube B, shall be so effectively supported that the rubber cannot, even under the highest pressures, move in any direction except toward the interior of the cell. This is accomplished, in part, by the brass piece *i*, which is concave at the bottom where it rests upon the stopper. The means by which the sides of the stopper are made rigid will be explained later, in connection with the procedure which is followed in setting up the cell for a measurement of pressure.

Since the holes through *h* and *i* are only a little larger than the manometer which passes through them, they must be placed upon the latter before the bulb *j* is blown and they cannot, thereafter, be removed.

The glass bottle *m* contains the water in which the cell is immersed. The cork ring *l*, which holds the cell in its place in the bottle, is split in a vertical direction to provide for the free passage of air.

6. The removal of the air from the porous wall of the cell, previous to the deposition of the membrane, has been effected, from the beginning of our work, by means of "electrical endosmose" and we have, as yet, discovered no reason for changing our procedure at this stage.

A narrow glass tube, with a side branch for the overflow, is passed through a stopper which is inserted in the cell at *e*. Through the vertical limb of this tube a stout platinum wire, which serves as a cathode, is lowered into the cell until it nearly touches the bottom. The cell is surrounded by a somewhat spacious cylinder made of platinum foil, which is employed as the anode. As the electrolyte, a very dilute solution of potassium sulphate is used.

The cell is filled with a 0.005 normal solution of the salt and then immersed in an ample supply of the same liquid, which is replenished from time to time to make good the water which passes through the porous wall and out of the horizontal tube above. The current pressure which we have found best suited to the removal of air is about 110 volts. The rate at which the water will pass through the cell wall varies greatly according to the texture. In very porous vessels the rate may exceed 1,000 cc. per hour, while in the case of the cells which were used for the present work, the endosmose amounted to only about 40 cc. per hour.

After 7 or 8 hours the salt solution is replaced by distilled water and the electrolysis is continued, with an occasional renewal of the water, until the conductivity of the liquid has been reduced to a minimum. The cell is then filled with and immersed in distilled water, which has been freed from air by boiling and it is not again disturbed until it is required for the deposition of the membrane.

The current pressure which is suitable for the deposition of a membrane depends on the character of the cell wall. The membrane which is formed on the inner wall of a highly porous vessel has always a low resistance and the higher the pressure of the current which is employed in its deposition, the lower is the resistance which can be secured. On the other hand, a membrane which is deposited in a cell of moderate, but uniform porosity may exhibit a resistance amounting to more than 100,000 ohms. This difference in cells, in respect to the resistance of the membranes which are deposited in them by the electrolytic process, appears to be due to the *endosmose* which, during the period of deposition, is always considerable in a highly porous cell, and less in a cell of closer texture. Apparently the rupturing and detaching effects of the in-rushing water are greater in the former case than in the latter.

Very porous cells are wholly unfit for the measurement of osmotic pressure and they can, at best, be utilized for qualitative demonstrations only. The membranes which are produced in them are, judging by our experience with more than 100 such cells, easily ruptured and, without exception, permit the escape of the dissolved substance.

The arrangement which is made for the deposition of the membrane in a cell to be used for the measurement of pressure is as follows: A glass tube, with an internal diameter of about 5 mm. and with two narrow horizontal side tubes attached to it, is passed through a rubber stopper which fits the mouth of the cell. One of the side tubes—the upper one—is occupied by the platinum wire which is connected with the electrode, while the other—the lower one—serves for the overflow from the cell. The interior electrode (the cathode) is a narrow platinum cylinder about 40 mm. in length. To provide for the renewal of the solution within the cell, a short piece of rubber tubing is slipped over the upper end of the vertical glass tube and through this the stem of a small separating funnel is pushed down until its lower end is on a level with the bottom of the electrode.

The exterior electrode (the anode) is a cylinder of copper.

The solution of potassium ferrocyanide which is placed within the cell and that of the copper sulphate, which surrounds it, are both of 0.1 normal concentration. The former is renewed every 5 or 10 minutes by admitting, through the separating funnel, a volume of the fresh solution which is about equal to the capacity of the cell. The object of the frequent renewal of the solution of potassium ferrocyanide is to prevent an accumulation of alkali within the cell, the presence of which appears to have an injurious effect upon the membrane. In the case of some of the new electrolytically deposited cobalticyanide membranes, which are now under investigation in this laboratory, this difficulty is obviated by adding acetic acid to the liquid in the cell.

A current pressure of 110 volts is well adapted to the deposition of the membrane in any cell which is fit for quantitative measurements, and we have used approximately this voltage in all of our experiments. On several occasions we have raised the voltage to 250, but the consequences were wholly unsatisfactory. No good membranes were obtained by the higher pressure and, on breaking open the cells, a greenish-black deposit was found upon the wall in the proper place for the reddish-brown copper ferrocyanide. It was concluded that the membrane is decomposed at the higher voltage. No such effect has been observed where a pressure not exceeding 110 volts had been used.

When the circuit is first closed the resistance is found to be very high, owing to the absence of electrolytes from the cell wall, which, of course, in the beginning, is filled with fairly pure water. The current, in a short time, commences to increase and soon reaches a maximum which, in cells of good quality, will not exceed 100 milliamperes. From this point it declines continuously to a minimum, which is usually, though not always maintained for a considerable time, when the current again begins to rise, indicating a diminishing resistance of the membrane.

We have selected as the proper moment for breaking the circuit the time when the current, after having been for a period at a minimum, begins to increase. The following record of one of our cells, taken after the membrane had begun to form, will illustrate the usual course:

Time.	Voltage.	Current.
9.20 A. M.	109.8	0.0021
9.30 "	110.0	0.0016
9.50 "	110.0	0.0012
10.10 "	109.2	0.0012
10.20 "	109.9	0.0012
10.30 "	110.0	0.0012
10.40 "	110.0	0.0012
10.50 "	110.1	0.0012
11.00 "	110.1	0.0012
11.10 "	110.1	0.0012
11.20 "	110.1	0.0012
11.30 "	110.1	0.0013
11.40 "	110.0	0.0014

The minimum is not always so long maintained as in the case cited above. It may last less than a half hour.

The probable excellence of a cell can be quite accurately estimated by its conduct during the membrane-forming period. If the resistance rises rapidly to a high maximum, which is maintained for a long time before a decline sets in, the cell may confidently be expected to render satisfactory service in the measurement of pressure. If, on the other hand, the resistance of the membrane rises slowly to a maximum, which is not high and which is not long maintained, the cell will probably—though by no means certainly—fail to give entirely satisfactory results. We have come to regard, in a general way, 100,000 ohms or more as a proper resistance for a membrane, though good measurements have been obtained with cells in which the resistance of the membrane did not exceed 30,000 ohms.

One of two courses is followed when a membrane has failed to develop the high resistance which is regarded as a guarantee of its subsequent good behavior. The cell is soaked over night in distilled water and again subjected to the membrane-forming process on the following day; or it is set up with a rather concentrated solution of sugar to which a quantity of potassium ferrocyanide has been added and immersed in water containing an equivalent amount of copper sulphate. The concentration which is adopted for the membrane-forming salts in the latter case is 0.1 normal.

The membrane which is deposited, after soaking the cell in water, often exhibits a higher resistance than the first one and the improvement is sometimes so great as to justify the setting up of the cell for a measurement of pressure. The second course is, however, much more certain to lead to a satisfactory result, provided the faulty conduct of the membrane is not due to the imperfect character of the porous wall, in which case it is impossible by either procedure to produce a serviceable cell.

When a new cell is to be prepared for the measurement of pressure, we expel the air in the manner already described and then proceed to deposit the first membrane. If its conduct during the latter operation is encouraging, the cell is washed with distilled water and set up with a half-normal, or even a normal solution of cane-sugar and allowed to develop pressure for several hours. The solution of sugar which is used in this first experiment with a cell is always made 0.1 N with potassium ferrocyanide and an equivalent amount of copper sulphate is added to the water on the outside. The purpose of adding the salts is two-fold. In the first place, if the structure of the porous wall is defective at any point, the location and also the character of the defect will be made apparent by the formation of colored spots or streaks upon the surface of the cell. In the second place, the membrane is usually strengthened by such treatment, apparently through a process of rupture in the weaker areas, which is followed by a mending of the rents.

In some cases, the pressure developed during the first trial of a cell rises rapidly and to a maximum which is known to be normal for the concentration of the solution. In others, the pressure develops more slowly and reaches the expected maximum very late or not at all. The former conduct is expected of a cell the membrane of which has a high resistance, and the latter of a cell with a membrane deficient in this respect.

Whatever the character of the result on the first trial may have been, the cell is taken down, washed and soaked for several hours in distilled water. It is then resubjected to the membrane-forming process, again washed and immediately thereafter it is filled and set up with a view to securing a measurement of osmotic pressure. However well the first membrane may have behaved, the second one usually surpasses it and it is not ordinarily necessary to repeat the treatment described above more than once before undertaking the measurement of pressure. These statements apply only to the cells which we have made in the laboratory. They do not hold good for the cells which have been made for us at the potteries. With the latter we have never succeeded in obtaining a measurement which we could regard as altogether satisfactory and it is in only a few of them out of many that we have been able to obtain anything more than very insignificant pressures. The reasons for this almost universal failure of the potters' products to render the service required of them, we shall hope to make clear after we have finished the investigation referred to at the beginning of this paper.

7. The setting up of the cell in a satisfactory manner is a feat of some difficulty. The manipulation, when the stopper carrying the manometer is inserted in the cell, is necessarily of a strenuous character and calls for both strength and endurance on the part of the one who undertakes it. At this point the coöperation of two persons is essential.

The first step to be taken is to prepare the manometer. If this has been used in an earlier experiment, the enlargement at *j* and the tube for some distance beyond will be filled with a solution which must be removed and the space vacated must be filled with the solution, the pressure of which is to be measured.

The manometer is tilted to one side until the mercury runs back to the upper end of the enlargement *j*. The liquid remaining in the bulb is then removed by means of a twisted fragment of absorbent paper and the space is filled, through a very fine tube, with the solution the pressure of which is to be measured. Finally, the open end of the tube is immersed in some of the same solution and the manometer is restored to the vertical position. If the solution removed and that to be used differ considerably in concentration, the operation is several times repeated.

The implement which is employed to enable the surplus liquid to escape when the stopper is crowded into the cell is made from a common round file. A deep groove is cut on one side of the flat, untempered end, which is afterwards heated and bent to the form of a rather open hook. The curved end is filed down and smoothed off until it resembles, in the proportions of its parts, the poison fang of certain serpents. A tool of this form is easily inserted between the rubber stopper and the glass at *e*, Fig. I., and, if properly made, it does not lacerate the former nor scratch the latter. It is also used for the introduction of air when the cell is opened at the end of an experiment.

The cell is wrapped with absorbent material to prevent soil-ing by the overflow from above and filled to the mouth with the solution. One of the operators holds the cell with one hand and manipulates the manometer with the other, the nut *h* resting, meanwhile, upon the back of the hand which holds the stopper. The duty of the other operator is to manipulate the "fang" until the stopper has been forced to a considerable depth into the glass tube and then to wrap the portion of the former which still remains outside of the latter. From the time when the stopper enters the tube until the nut *h* is brought down upon it and secured by the collar *g* there must not be the slightest relaxation of the pressure, otherwise air will enter the cell through the groove in the tool, or—after the removal of the tool—the mercury column will recede and allow some of the air in the manometer to escape around the bend into the bulb above.

A method of supporting the portion of the stopper remaining above the tube B, which we have found quite satisfactory, is to wrap it tightly with a strip of the sticky insulating tape which is used in electrical construction. It is for the purpose of making room for this that the diameter of the cavity in the bottom of the nut *h* is made a little greater than that of the stopper. The strip of tape is cut wide enough to cover the whole of the exposed portion of the stopper *k* and long enough to pass several times around it. After the removal of the tool, operator No. 2 seizes the stopper and holds it in place, while No. 1 removes his fingers to the top of the stopper to make room for the winding which is now attended to by No. 2. This finished, No. 2 again seizes the stopper and holds it until No. 1 has brought the nut *h* down to its place, when No. 2 turns the collar *g* until a rise of the mercury column indicates that the cell is safely closed.

Any failure to manipulate correctly while closing the cell is sure to be followed by serious trouble. The stopper must be driven quite deeply into the tube, otherwise it will be tipped to one side under high pressures and may, in consequence of such displacement, break the manometer or even permit the escape of some of the solution. Again, if the support given to the stopper by the tape is insufficient it will "bulge" in the upper part and perhaps be driven out of the cell.

After closing the cell and placing it in the bottle *m*, the mercury in the manometer usually sinks for a time, remains stationary for a while and then begins to rise. This phenomenon is due to the fact that, while closing the cell, it is held in the hand and is warmed to a temperature above that of the water in the bottle. The shrinkage in the volume of the solution which follows the plunging of the cell into the colder water is not immediately compensated by the inflow of water through the membrane. After a time the two processes become equal and the mercury stands still for a few moments. Soon thereafter the flow of water into the solution exceeds the contraction of the latter and the mercury starts upward, in consequence of increasing pressure in the cell. When the mercury is seen to rise, the nut *h* is grasped with the wrench and the collar *g* is turned with the hand until a considerable additional pressure has been brought upon the solution. The purpose of this is to force the stopper somewhat further into the cell and to make the portion of it which is outside of the cell so rigid that no internal pressure can drive the lower end of the stopper upwards and out of its place. One who has had some experience in this manipulation can readily tell when the stopper is sufficiently rigid by the resistance which it offers when the collar is turned.

The pressure which is brought upon the contents of the cell, in the manner described, is never made equal to the osmotic pressure, owing to the danger of rupturing the membrane, though, in the case of concentrated solutions, it is sometimes carried to 14 or 15 atmospheres before it is felt to be safe to leave the stopper to itself.

8. In order to obtain correct determinations of osmotic pressure, the closest attention must be given to temperature conditions at several points. In the earlier stages of our work we were not so much impressed with the importance of this as we afterwards came to be and certain precautions, which should have been taken, were more or less neglected.

In the solutions upon which we have experimented, the relations of dissolved substance to solvent were *weight* relations exclusively, the unit weight of the water being, in all cases, 1000 grams, or that mass of the solvent the volume of which is 1 liter at the temperature of maximum density ; while the unit for the sugar was a gram-molecular weight (342.22 grams), or some decimal part thereof. The reason for selecting such proportions will appear later, when the significance of the results is discussed. The relations being those of weight only, it was a matter of no concern at what temperature the solutions were made, but the case is different when the cell is filled and closed. At that time the solution should have, as nearly as possible, the temperature at which the pressure is to be measured, since, if it has any other temperature the cell will contain, when closed, either too much or too little of the dissolved substance. The bearing of this fact upon one feature of the manipulation while setting up the cell is of some importance. The cell must then be tightly held in the hand for several minutes and the heating effect upon the solution within may be considerable unless measures are taken to protect the cell by wrapping it with non-conducting material. This precaution was neglected in our earlier experiments, but not in the later ones.

The thermal manifestations which have given us the most trouble are what we shall call *thermometer effects*. When a cell, in which the full pressure of the solution has been developed, is standing in a room where the temperature is fluctuating, the following movements of the mercury column in the manometer will be noticed : If the temperature of the room falls, the mercury column also falls, but always to a point *below* that which is normal for the concentration of the solution in the cell. If, after falling for a time, the temperature of the room becomes stationary, the mercury will rise again and if it remains constant for a sufficiently long time, the mercury will rise to the point which is normal for the concentration of the solution and there it will remain as long as the temperature conditions are unchanged. If, on the other hand, the temperature of the room rises, the mercury column also rises, but always to a point *too high* for the concentration of the solution. If, after rising for a time, the temperature becomes stationary, the mercury again falls and always to the point which is normal for the solution, provided no new fluctuations of temperature set in.

The explanation of these phenomena is obvious. When the temperature is falling, the solution and the mercury enclosed in the cell contract *faster* than the water can get through the membrane for the purpose of maintaining the pressure which is normal to the solution and the mercury column, therefore, descends to an abnormally low point in the manometer. The solution, however, continues to take in water and, eventually, the proper degree of pressure is restored if the minimum temperature, after a fall, is sufficiently long maintained. On the other hand, when the temperature of the room rises, the enclosed solution and the mercury expand *faster* than the water is expelled from the cell and the consequence is that the mercury column in the manometer rises to a point which is abnormally high for the concentration of the solution, but the expulsion of water continues after the maximum temperature has been reached and the mercury begins to fall. If the maximum, after a rise of temperature, is sufficiently long maintained, the *over-pressure* will be reduced to the normal and the mercury will then become stationary.

This conduct on the part of the cell is very striking when the fluctuations of temperature are rapid and of considerable magnitude and it may lead to large errors in the determination of osmotic pressure. It is only when the changes of temperature are exceedingly slow that the passage of water in either direction, through the membrane, can keep pace with the contraction and expansion of the contents of the cell and the degree of exactness which can be secured in the measurement of osmotic pressure obviously depends, to a large extent, upon the weight which is attached to this fact.

In this connection we wish to speak of certain objections to a method of measuring osmotic pressure which has sometimes been practiced. The attempt has been made, on several occasions, to ascertain the pressure of solutions by bringing mechanical pressure to bear upon the contents of the cell until the mercury in the manometer rises to the highest point, becomes stationary and then begins to fall. A minor objection to such procedure is the fact that it is not possible to ascertain whether the observed conduct of the mercury column, in the second and third stages, is due to a rupture of the membrane or to a *supposed* equilibrium between the mechanical and the osmotic pressures, which is afterwards disturbed by a slight excess of the former just at that point of time when the mercury begins to fall. The membrane is very liable to rupture under the strain of large and irregular accessions to the pressure upon it and it is not impossible that some of the measurements made by the method in question are, in reality, measurements of the strength of the membrane or of the support which is given to it by the porous wall behind.

A second and more serious objection to the method is the fact that pressures measured in this way are probably *over-pressures* in all cases where the membrane is not broken, owing to the slowness with which any excess of water in the cell is expelled. The mercury column should come to a standstill when the increase of the mechanical pressure which is brought upon the solution is in equilibrium with the rate of expulsion of water from the cell, and it appears to the authors that this state is not likely to be reached until the mechanical pressure considerably exceeds the osmotic pressure. This would not be true, of course, if the solution could instantaneously discharge its excess of water when subjected to a mechanical pressure superior to its osmotic pressure. Since it cannot do so, but, on the contrary, requires a considerable time for the completion of the process, the *lowest* point to which the mercury *falls* after a rise, rather than the highest point which it reaches in the ascent, should be taken as the gauge of the osmotic pressure.

At first our cells were set up, without any external protection, in a room which was subject to the usual daily and nightly fluctuations of temperature, except that some measures were taken to moderate the extremes and to avoid very rapid changes of temperature. But the thermometer effects, of which we have spoken, were so pronounced that we began to protect the cells by placing them in boxes which were both lined and covered with flannel cloth and were opened only for the purpose of determining the pressure. In this way the thermometer effects were considerably reduced, but not to a negligible magnitude. Later we adopted, and are still using, the arrangement which is shown in Figs. III., IV. and V. This consists of a box, Fig. III., having two doors, *a* and *c*, with an air space between them. The former, *a*, has a narrow plate-glass window, *b*, through which the height of the mercury in the manometer and also of the thermometers can be read without opening the inner door. The outer door, *c*, has, in its center, the smaller door, *d*, which is of the same size as the window, *b*. When a reading is to be made, it is necessary only to open the small door, *d*. The walls of the box are double and the space between is filled with inch-thick hair felt. Fig. IV., gives a sectional view of the box from front to back, in which the wooden walls and the hair between are designated by *a* and *b*, respectively. The small door, which is opened for the purpose of observing the manometer and thermometers, is indicated by *f* and the glass window by *i*. In the front part of the box there are two woolen curtains, *g*, which can be drawn aside or closed without opening the box. One of these is behind the inner door and the other between the two doors, *a* and *a*, shown in Fig. III. In the top of the box there are two holes, *e*, *e*, through which thermometers are lowered into the space below. There is also a small window, *d*, in the top, which was expected to serve for the illumination of the interior from above, but this has not been utilized for that purpose, owing to the effect of its use upon the temperature conditions within the box. The space below the window, *d*, is covered with the felt, *c*. Fig. V., gives the side-to-side sectional view of the box.

The arrangement, as described, was expected to render the changes of temperature so exceedingly slow as to eliminate the thermometer effects, but in this we were disappointed. They were smaller than before, but still not wholly negligible. Accordingly, the whole of the interior of the box, except in front of the glass window *b*, was lined with felt covered with flannel.

When the cell, after closing, is to be put in the box, a ther-

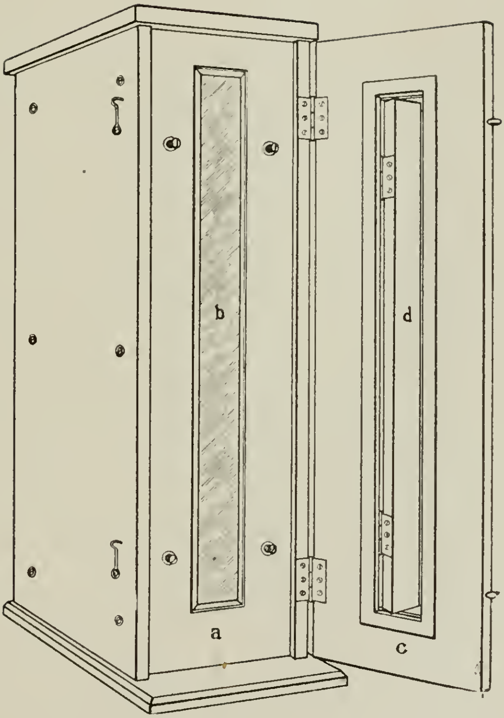

Fig. III.

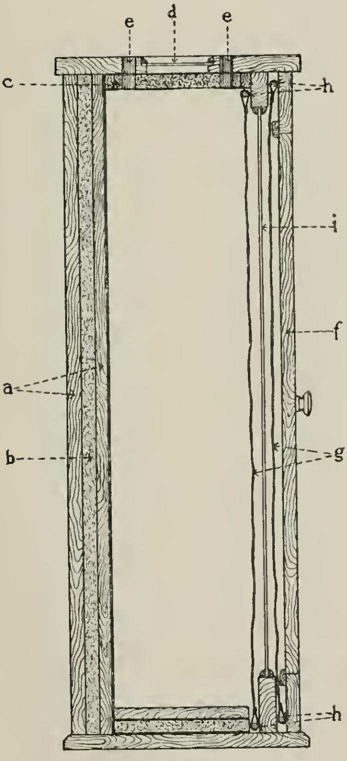

Fig. IV.

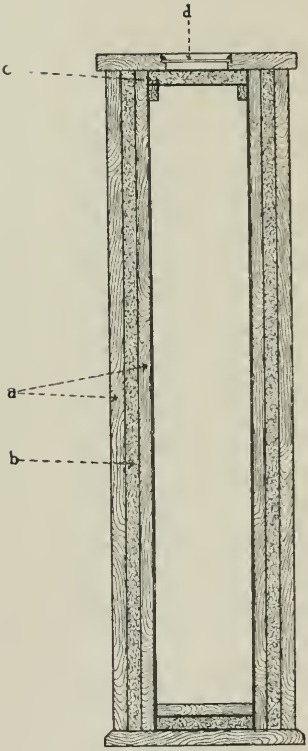

Fig. V.

mometer is strapped to the bottle *m*, Fig. I., with its bulb in contact with the glass. The cell, with the thermometer in place, is wrapped with a piece of felt, which is tied to the bottle. The protecting covering extends from the bottom of the bottle to the top of the nut *h*, Fig. I., but does not include any portion of the manometer. The space which is left between the upper, narrow portion of the cell and the felt is filled with hair.

After packing the cell in the manner described, it is placed on a felt base in the box and adjusted, with the aid of the telescope and plumb lines, until the manometer is vertical. By this time the osmotic pressure will have increased to such an extent that the further rise of the mercury in the manometer cannot sensibly affect its level in the bulb. Accordingly, certain readings are made for use in the later computations of pressure. They are the following: (1) The vertical distance between the level of the water in the bottle and that of the mercury in the manometer bulb; (2) the vertical distance between the height of the mercury in the bulb and the lines of reference on the manometer; (3) the vertical distance between the lines of reference on the manometer. Readings 1 and 2 are used in the subsequent computations of the pressure of the liquids in the manometer tube. If the distance between the top of the manometer and the upper line of reference has been ascertained previously, the only reading—except for temperature—which it is necessary to make when the pressure is to be determined is the distance between the upper line of reference and the top of the mercury column.

The whole interior of the box, from the bottom to a point half way up the manometer, or even higher, is carefully packed with hair, narrow strips of covered felt, somewhat longer than the internal width of the box, being used for the front retaining wall. The use of these strips, instead of one wide pad, for the front makes it possible to build up the packing by stages and, therefore, more carefully and conveniently than it could otherwise be accomplished. The thermometer which is used to register the temperature of the cell is a very long one, so that the portion of the scale which is to be read through the window is in sight above the packing.

In Figs. IV., and V., only one thickness of felt is shown at the top of the box. There are, in reality, as many of these as are necessary to fill the space between the top of the manometer and the upper end of the box. Through holes in these, two long thermometers are pushed down until their bulbs are opposite the midway point of the column of air in the manometer. When the temperature is to be ascertained, the thermometers are drawn upwards until the mercury appears in sight above the top of the box.

All three of the thermometers which are used in the box are graduated to 0°.2.

When readings are to be made the curtains *g*, Fig. IV., are drawn aside and the small door *d*, Fig. III., is opened. If the light within is insufficient, that from an electric lamp without is thrown in from a distance during the final adjustment of the telescope.

9. Soon after beginning the measurement of the osmotic pressure of cane-sugar, under conditions which gave to the results a considerable degree of precision, it became apparent that the *mass of the solvent* plays a part which appears to have been unsuspected hitherto. We found—or *appeared* to discover—that a gram-molecular weight of the substance, dissolved in water and diluted to a liter volume, is not the normal standard for osmotic pressure. On the other hand, *when we dissolved a gram-molecular weight of cane-sugar (342.22 grams) in 1,000 grams of water, i. e., in that mass of the solvent which has the unit volume, 1 liter, at the temperature of maximum density—we found its osmotic pressure, at about 20°, in quite close accord with the pressure which a gram-molecular weight of hydrogen would exert, at the same temperature, if its volume were reduced to 1 liter, i. e., to that volume which the unit mass of the solvent has at the temperature of greatest density.*

The osmotic pressures of solutions ranging in concentration from 0.05 to 1 gram-molecular weight of sugar, in 1,000 grams of water, have since been measured and the results are all reasonably in accord with the hypothesis of van 't Hoff, that *osmotic pressure obeys the laws of gases*, provided we accept, as the standard for the solvent, the fixed mass of 1,000 grams of water. These results, together with most of the data employed in calculating them, are presented in the latter part of this paper.

Our solutions, as stated above, were all made by dissolving a gram-molecular weight of cane-sugar, or some decimal part thereof, in 1,000 grams of water. The sugar used was "rock candy." The absolute purity of the material cannot be guaranteed, but several determinations of the carbon and hydrogen in it were made and the results were quite satisfactory. It was also tested for the products of inversion and found to be free from them.

The weights of the sugar and water were not corrected for displacement of air, hence they are slightly erroneous.

The solutions, made by dissolving a gram-molecular weight of sugar, or some decimal part of the same, in 1,000 grams of water, we shall call *weight-normal* to distinguish them from *volume-normal* solutions, *i. e.*, those which are made by dissolving the given weight of substance in water and diluting to a liter volume.

The specific gravities, at 20°, of the various concentrations of solution, the pressures of which were measured, were carefully determined with the use of Sprengel pycnometers and a constant bath. These are given in the table which follows, together with the equivalent *volume-normal* concentration of the solutions. There is also given, in the last column of the table, the true weight-normal concentrations of our solutions. The difference between the corresponding values in the first and last columns is the measure of the error resulting from a failure to correct the weights of sugar and water for air-displacement. The error is not large and may well be neglected in a first series of experiments. When the work is repeated, this and several other small errors pertaining to the present results will be excluded.

Table III.—Weight-Normal Solutions of Cane-Sugar.

Weight-normal concentration (uncorrected).	Specific gravity (in air) at 20° (uncorrected).	Grams of sugar in 1,000 grams of water (uncorrected).	Grams of sugar in 1 liter at 20° (uncorrected).	Equivalent volume-normal concentration (uncorrected).	Weight-normal concentration, corrected for air displacement.
0.05	1.006538	17,111	16.933	0.04948	0.04997
0.10	1.012920	34.222	33.518	0.09794	0.09995
0.20	1.025328	68.444	65.679	0.19192	0.19990
0.25	1.031240	85.555	81.271	0.23748	0.24988
0.30	1.037120	102.666	96.563	0.28216	0.29986
0.40	1.048460	136.888	126.280	0.36886	0.39981
0.50	1.059385	171.110	154.780	0.45228	0.49977
0.60	1.069858	205.332	182.240	0.53252	0.59972
0.70	1.079935	239.554	208.690	0.60981	0.69968
0.75	1.084805	256.665	221.550	0.64739	0.74966
0.80	1.089603	273.776	234.170	0.68428	0.79963
0.90	1.098920	307.998	258.750	0.75610	0.89959
1.00	1.107915	342.222	282.45	0.82534	0.99955

On taking down the cells after the measurement of pressure, the contents were immediately tested for inversion and evidence of the probable presence of invert sugar were found in all cases. In the more dilute solutions it did not amount to a quantity which could be determined and the evidence of its presence, even, was frequently of a dubious character. In the more concentrated solutions, on the other hand, the inversion which had taken place was of sufficient magnitude to permit of a quantitative estimation and, in such cases, the pressures observed have been corrected by deducting the theoretical osmotic pressure of one-half of the invert sugar which was found.

Whenever a cell was filled a portion of the solution was set aside in a closed vessel and, when the cell was opened at the close of the experiment, the contents were compared with the reserved portion with respect to the amount of inversion which had taken place in the interval, it was found, in every instance, that the inversion in the liquid taken from the cell was greater than in the other portion of the same solution. If the evidence of inversion in the dilute solutions was of a doubtful character in the one case, it was still more so, or altogether lacking in the other, and the inversion in the reserved portions of the more concentrated solutions did not, in any instance, reach an amount which could be quantitatively estimated. It is, however, not safe to conclude that the greater *pressure* to which the contents of the cell were subjected was the sole cause of the greater inversion.

In all of our experiments we have added to the sugar solutions a small amount of potassium ferrocyanide and, to the water in which the cells were immersed, an equivalent amount of copper sulphate. The purpose of doing so has already been explained. The quantity of the former which was added to every solution of sugar was 0.0846 gram per 100 grams of water, while the copper sulphate added to the water outside of the cell amounted to 0.12488 gram per 100 grams of water. These quantities, if the salts are completely dissociated, are osmotically equivalent and their presence should not, therefore, affect the measurements of pressure. The greater inversion which was observed in the cell cannot, of course, be ascribed to the ferrocyanide, since the reserved portions of the solutions contained the same amount of it.

The method which was employed to determine the extent of the inversion was as follows: 0.5 cc., sometimes only 0.3 cc., of freshly prepared Fehling's solution was diluted with water and heated to the boiling-point. A measured portion of the sugar solution was then added and the liquid was boiled exactly 2 minutes. The experiment was repeated with fresh Fehling's solution and with smaller or larger quantities of the sugar solution, according as the color had, or had not wholly disappeared in the previous trial, until the exact volume of sugar solution required for decolorization had been ascertained.

We have not tested the accuracy of the method further than to satisfy ourselves that freshly prepared solutions of cane-sugar do not, under the same conditions, reduce Fehling's solution.

If a gram-molecular weight of a substance, dissolved in 1,000 grams of water, exerts an osmotic pressure equal to the pressure of a gas when a gram-molecular weight of it is reduced to a volume of 1 liter, and if osmotic pressure, like gas pressure, obeys the law of Gay-Lussac, then the osmotic pressure of a weight-normal solution, at 0°, is 22.488 atmospheres and, at any higher temperature it is $22.488 + \frac{22.488}{273}$, or $22.488 + 0.0824t$ atmospheres.

Accordingly, if the osmotic pressure, P, which any solution is found to exert at the temperature t, is divided by $22.488 + 0.0824t$, the quotient is the concentration of the solution in terms of the weight-normal system, that is

$$\frac{P}{22.488 + 0.0824t} = \text{the weight-normal concentration of any solution.}$$

To find the molecular weight, M, of any substance from the osmotic pressure, P, which a known weight of it, W, exerts when dissolved in 1,000 grams of water, we have only to ascertain the value M in the proportion

$$\frac{P}{22.488 + 0.0824t} : 1 :: W : M.$$

The formula for the calculation of molecular weight from osmotic pressure is, therefore,

$$M = \frac{W(22.488 + 0.0824t)}{P}.$$

Our measurements have been tested by this formula and the results are given in the last column of each of the following tables.

The estimated pressure of 22.488 atmospheres for a gas, when the volume of a gram-molecular weight of it is reduced to 1 liter at 0°, is based on the value given by Morley for the weight of a liter of hydrogen, under standard conditions of temperature and pressure, at latitude 45°. This value is 0.089873 gram and, corrected to the latitude of this place, it becomes 0.089826 gram. Accepting 1.01 as the atomic weight of hydrogen, we have $\frac{2.02}{0.089826} = 22.488$. The value 22.443 is slightly more correct, but the difference between the two is not sufficient to affect materially either the theoretical pressure given in column XI. of the tables or the molecular weights, calculated from osmotic pressure, which are recorded in column XIII.

It is hardly necessary to state that the deviations from the laws of Boyle and Gay-Lussac, which are observed in the conduct of air under pressure, have not been taken into account in our computations. Such refinements would, obviously, be inappropriate until after a better control has been obtained of the conditions under which the work is done, especially of temperature conditions.

The pressure of the atmosphere at the time the readings were made has been deducted before computing the values recorded in column X. of the tables.

0.05 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 17.111 grams.

Specific gravity of solution at 20° = 1.00653.

Grams of sugar in 1,000 cc. at 20° = 16.933.

Concentration of solution according to the *volume-normal* standard = 0.04948.

Cell used, A.

It had previously been employed to measure the pressure of a 0.10 weight-normal solution. When taken down it was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

March 27, 1905.

Time.	Voltage.	Current.	Resistance.
10.35 A. M.	109.3	0.0200	5465
10.40 "	109.3	0.0029	37690
10.50 "	109.3	0.0022	49690
11.00 "	109.3	0.0016	68330
11.40 "	109.3	0.0013	84077
12.15 P. M.	109.8	0.0012	91500
12.45 "	109.7	0.0011	99730
1.00 "	110.0	0.0010	110000
3.15 "	110.0	0.0011	100000

Manometer No. 3 was used.

Table IV.—Record of Observations.

(Experiment I. with 0.05 weight-normal solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 27, 1905.						Atmospheric pressure not deducted.		The inversion was very slight and could not be determined.				
4.30 P. M.	441.6	666.4				1.73						
8.30 "	441.8	668.5				2.04						
March 28.												
8.45 A. M.	441.6	645.7	20°.5	19°.35	0.35 Atmosphere.	2.26	190.42		1.23	1.21	0.02	336.3
12.00 M.	441.6	644.45	20°.36	20°.04		2.27	190.42		1.23	1.21	0.02	336.1
4.15 P. M.	441.65	639.6	20°.6	21°.55		2.30	185.49		1.28	1.21	0.07	323.3
6.00 "	441.55	637.25	20°.8	22°.26		2.34	182.65		1.31	1.21	0.10	316.1
9.15 "	441.65	634.80	21°.2	22°.32		2.37	179.89		1.34	1.21	0.13	309.4
March 29.												
8.30 A. M.	441.7	639.4	21°.16	20°.4		2.32	185.49		1.28	1.21	0.07	323.9
12.00 M.	441.66	640.65	20°.98	20°.61		2.31	187.43		1.26	1.21	0.05	327.5
3.00 P. M.	441.60	639.82	21°.1	21°.45		2.32	185.49		1.28	1.21	0.07	323.8
5.30 "	441.63	637.9	21°.24	22°.05		2.34	183.53		1.30	1.22	0.08	319.7
												324.0

Number of calibration units of air, under standard conditions, in the manometer = 357.99.

The cell was set up at 3.45 P. M., March 27, with a 0.05 weight-normal solution which contained 0.0846 gram of $K_4Fe(CN)_6.3H_2O$ per 100 grams of H_2O. The water on the outside contained 0.12488 gram $CuSO_4.5H_2O$ per 100 grams of water. The initial pressure was 1.6 atmospheres.

Values Used in Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to 1 liter volume.

Comments.

The minimum and maximum difference between pressures found and calculated are 0.02 atmosphere and 0.13 atmosphere, respectively (column XII.). These, though seemingly not very far apart, correspond to a large difference in molecular weights, *i. e.*, 26.9 (column XIII.).

It is to be noted that, when molecular weights are determined by osmotic pressure, the accuracy of the results increases with the concentration of the solutions; in other words, a given error of measurement diminishes in importance as the value of W in the formula $M = \frac{W(22.488 + 0.0824t)}{P}$ increases.

0.05 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 17.111 grams.

Specific gravity of solution at 20° = 1.00653.

Grams of sugar in 1,000 cc. at 20° = 16.933.

Concentration of the solution according to the *volume-normal* standard = 0.04948.

Cell used, A.

It was soaked in water over night after Experiment I. with a 0.05 weight-normal solution and then subjected to the membrane-forming process.

Record.

March 30, 1905.

Time.	Voltage.	Current.	Resistance.
9.20 A. M.	109.8	0.0021	52280
9.30 "	110.0	0.0016	68730
9.50 "	110.0	0.0012	91670
10.10 "	109.2	0.0012	91000
10.20 "	109.9	0.0012	91590
10.30 "	110.0	0.0012	92670
10.40 "	110.0	0.0012	91670
10.50 "	110.1	0.0012	91750
11.00 "	110.1	0.0012	91750
11.10 "	110.1	0.0012	91750
11.20 "	110.1	0.0012	91750

Manometer No. 3 was used.

Number of calibration units of air = 357.99.

The cell was set up at 12.00 M., March 30, with a 0.05 weight-normal solution, the solution containing the same proportion of $K_4Fe(CN)_6.3H_2O$ as in Experiment I. and the water without the same proportion of $CuSO_4.5H_2O$ as in Experiment I. The initial pressure, uncorrected, was 1.8 atmospheres.

Values Used in Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488 atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Comments.

The average of the molecular weights calculated from the osmotic pressures observed in Experiment I., with a 0.05 weight-normal solution, is 324.0, while the corresponding value in the case of Experiment II. is 331.7. These numbers are decidedly low for the molecular weight of cane-sugar (18.22 and 10.52 units, respectively), but it is to be observed that these were among the first experiments which were made and that, at the time of making them, we had not begun to employ the precautions which were afterwards taken to avoid rapid changes of temperature.

Table V.—Record of Observations.

(Experiment II. with 0.05 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 30, 1905.												
2.30 P. M.	436.70	677.4				1.91		Inversion insufficient for quantitative measurement.				
5.30 "	436.25	665.14	21°.2	21°.87	0.35 Atmosphere.	1.99						
8.30 "	436.20	665.10	21°.1	21°.87		2.11						
March 31.						Atmospheric pressure not deducted.						
8.30 A. M.	436.23	645.23	20°.9	19°.5		2.21	197.78		1.16	1.21	—0.05	357.1
12.00 M.	436.52	642.77	20°.8	20°.43		2.23	193.51		1.20	1.21	—0.01	345.1
5.30 P. M.	436.63	637.17	20°.9	21°.55		2.30	187.43		1.26	1.21	0.05	328.7
8.30 "	436.15	633.70	20°.2	22°.00		2.32	184.53		1.29	1.21	0.08	320.3
April 1.												
8.30 A. M.	436.45	634.76	20°.8	19°.99		2.32	186.45		1.27	1.21	0.06	326.1
2.45 P. M.	436.63	634.28	20°.73	20°.82		2.32	184.53		1.29	1.21	0.08	320.9
4.50 "	436.35	634.00	20°.8	20°.90		2.32	185.49		1.28	1.21	0.07	323.5
												331.7

It is to be noted, further, that in very dilute solutions a small absolute error in the measurement of pressure corresponds to a large error in the estimated molecular weight. For example, a mistake of 0.1 atmosphere in the measurement of the pressure of a 0.05 weight-normal solution of cane-sugar gives an error of 30.4 units in the molecular weight.

0.10 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 34.222 grams.

Specific gravity of solution at 20° = 1.01293.

Grams of sugar in 1,000 cc. at 20° = 33.518.

Concentration of the solution according to the *volume-normal* standard = 0.09794.

Cell A. It had been used with a 0.25 weight-normal solution. It was taken down March 20, 1905, soaked over night of March 20 and subjected to the membrane-forming process March 21.

Record.

March 21, 1905. Started at 2.55 P. M.

Time.	Voltage.	Current.	Resistance.
3.00 P. M.	107.2	0.0023	46610
3.15 "	107.0	0.0016	66870
3.22 "	107.0	0.0013	82310
3.45 "	107.3	0.0013	82540
4.00 "	107.3	0.0013	82540
4.15 "	107.3	0.0012	89420
4.30 "	107.0	0.0012	89165

Manometer No. 3 was used.

Number of calibration units of air in the manometer = 357.99.

The cell was set up at 4.50 P. M., March 21, with a 0.10 weight-normal solution.

The solution within contained the usual proportion of $K_4Fe(CN)_6.3H_2O$, *i. e.*, 0.0846 gram per 100 grams of H_2O, and the water without the usual amount of $CuSO_4.5H_2O$, *i. e.*, 0.12488 gram per 100 grams of H_2O. Initial pressure = 1.2 atmospheres.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Comments.

This experiment illustrates well the effect of fluctuating temperature upon the measurement of osmotic pressure. The night of March 23 was cold and the temperature of the room fell to a low point. The consequence is apparent from the readings which were made the following morning.

At this time the only precaution which was taken to protect the cell consisted in placing it in a wooden box which was lined and covered with woolen cloth. This provision was found wholly inadequate whenever the temperature at night differed considerably from that of the preceding and following days.

A mistake of 0.1 of an atmosphere, in the measurement of the osmotic pressure of a 0.1 weight-normal solution, produces an error of 15.2 units in the estimated molecular weight of cane-sugar.

0.10 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 34.222 grams.

Specific gravity of solution at 20° = 1.01293.

Grams of sugar in 1,000 cc. at 20° = 33.518.

Concentration of the solution according to the *volume-normal* standard equal 0.09794.

Cell A was used. It was soaked in distilled water from 8.30 A. M. to 3.00 P. M., after use in Experiment I., with a 0.10 weight-normal solution and then subjected to the membrane-forming process.

Table VI.—Record of Observations.

(Experiment I. with 0.10 Weight-Normal solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecuar weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 21, 1905.												
5.50 P. M.	402.73	682.3			0.45	1.54 Atmospheric pressure not deducted		The inversion was insufficient to permit of a quantitative determination.				
March 22.												
9.00 A. M.	402.70	552.7	16°.0	15°.87	Atmosphere.	2.99						
12.00 M.	402.50	538.6	17°.7	18°.96		3.30						
4.00 P. M.	402.55	527.56	19°.9	21°.26		3.56	116.65		2.52	2.41	0.11	327.7
5.30 "	402.40	528.00	20°.1	20°.98		3.54	117.31		2.50	2.41	0.09	330.5
March 23.												
9.00 A. M.	402.54	544.48	15°.62	14°.25		3.17	135.65		2.07	2.37	[−0.30!]	[393.0!]
12.00 M.	402.70	536.40	16°.5	16°.9		3.35	126.59		2.27	2.38	−0.11	359.5
2.45 P. M.	402.50	527.80	18°.9	19°.1		3.57	117.6		2.49	2.40	0.09	330.4
												337.0

Table VII.—Record of Observations.

(Experiment II. with 0.10 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 24, 1905.												
5.40 P. M.	440.9	660.1				2.11 Atmospheric pressure not deduct'd		The inversion was insufficient to permit of quantitative determination.				
8.30 "	440.9	614.6	20°.15	20°.2		2.63						
March 25.												
8.30 A. M.	441.1	574.0	18°.5	16°.78	0.45 Atmosphere.	3.37						
12.00 M.	441.0	571.48	18°.54	18°.42		3.46	122.92		2.36	2.40	—0.04	348.0
3.00 P. M.	440.9	568.5	18°.64	19°.46		3.49	119.71		2.44	2.40	0.04	336.9
5.00 "	440.1	566.75	18°.9	19°.85		3.52	118.74		2.46	2.40	0.06	334.5
8.45 "	440.9	565.9	19°.18	19°.86		3.56	117.19		2.50	2.40	0.10	329.4
March 26.												
10.30 A. M.	441.0	568.2	18°.5	18°.92		3.51	118.70		2.46	2.40	0.06	334.0
12.30 P. M.	441.1	568.19	18°.5	18°.45		3.51	119.74		2.44	2.40	0.04	336.8
												336.6

Record.

March 24, 1905.

Time.	Voltage.	Current.	Resistance.
3.00 P. M.	108.0	0.0100	10800
3.15 "	108.0	0.0022	49090
3.25 "	108.0	0.0016	67500
3.40 "	108.0	0.0013	83085
4.00 "	108.0	0.0013	83085
4.10 "	108.0	0.0012	90000
4.20 "	107.5	0.0012	89585

The manometer was No. 3.

Number of calibration units of air = 357.99.

The cell was set up at 5.30 P. M., March 24, 1905, with a 0.10 weight-normal sugar solution containing the usual amount of $K_4Fe(CN)_6.3H_2O$.

The initial pressure, uncorrected, was 2.11 atmospheres.

Values Used in Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

0.20 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 68.444 grams.

Specific gravity of solution at 20° = 1.02530.

Grams of sugar in 1,000 cc. at 20° = 65.679.

Concentration of the solution according to the *volume-normal* standard = 0.19192.

Cell B was used for the first time in this experiment for the measurement of pressure. It had been set up the previous day with a 0.20 weight-normal solution and allowed to develop pressure. The following record was made. Set up at 5.15 P. M., April 10 :

Record.

April 10, 1905.	Pressure uncorrected.	Temperature.
8.30 P. M.	4.95	20°.40
April 11.		
9.00 A. M.	4.84	19°.5
12.00 M.	4.89	19°.5
3.00 P. M.	4.98	19°.8
5.00 "	5.04	20°.2

The cell was taken down, soaked over night in distilled water and again subjected to the membrane-forming process on April 12.

Record.

April 12, 1905.

Time.	Voltage.	Current.	Resistance.
9.45 A. M.	110.6	0.0025	44240
9.50 "	110.6	0.0021	52670
10.00 "	110.7	0.0017	65120
10.05 "	110.8	0.0014	79140
10.15 "	110.7	0.0013	85155
10.25 "	110.7	0.0013	85155
10.35 "	110.7	0.0013	85155
10.45 "	110.7	0.0012	92250
10.55 "	110.7	0.0012	92250
11.05 "	110.7	0.0013	85155
11.15 "	110.7	0.0014	79140

The cell was set up at 11.40 A. M., April 12, with a 0.20 weight-normal solution containing the usual quantity of potassium ferrocyanide. Initial pressure = 4.01 atmospheres.

Manometer No. 3 was used after fourth filling.

Number of calibration units of air = 399.05.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488 atmospheres of pressure for a gram.molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

Comments.

Only two cells were used in this work. They are designated by the letters A and B. The latter was used for the first time in this experiment. Attention is called to the rapidity with which the pressure approached a maximum. The cell was set up at 11.40 A. M. and at 3.00 P. M. the pressure had reached 4.75 atmospheres (corrected), the theoretical pressure at the same temperature being 4.85 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.2 weight-normal solution produces an error of 7.6 units in the estimated molecular weight of cane-sugar.

Table VIII.—Record of Observations.

(Experiment I. with 0.20 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of the air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 12, 1905.												
3.30 P. M.	457.12	538.53	21°.75	21°.30	0.497 Atmosphere.	5.82 Atmospheric pressure not deducted.	75.93	Insufficient for quantitative determination.	4.75	4.85	—0.10	349.8
5.00 "	457.00	538.33	21°.70	21°.37		5.84	75.90		4.75	4.85	—0.10	349.8
8.30 "	457.35	538.00	21°.53	21°.25		5.89	75.23		4.80	4.85	—0.05	345.6
April 13.												
8.30 A. M.	457.35	537.91	20°.10	18°.87		5.89	75.75		4.77	4.83	—0.06	346.4
12.30 P. M.	457.35	538.00	19°.64	18°.70		5.92	75.89		4.75	4.82	—0.07	347.3
3.00 "	447.15	537.85	19°.68	19°.30		5.89	75.71		4.77	4.82	—0.05	345.9
5.00 "	457.06	537.62	19°.70	19°.70		5.90	75.54		4.78	4.82	—0.04	345.2
												347.1

0.20 Weight Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 68.444 grams.

Specific gravity of solution at 20° = 1.0253.

Grams of sugar in 1,000 cc. at 20° = 65.679.

Concentration of the solution according to the *volume-normal* standard = 0.019192.

Cell A was used. It had been previously set up with a 0.90 weight-normal solution, but after a pressure of 14.9 atmospheres had been developed the stopper was dislodged. The cell was then taken down, soaked in distilled water over night and again subjected to the membrane-forming process.

Record.

April 25, 1905.

Time.	Voltage.	Current.	Resistance.
3.21 P. M.	110	0.0030	56667
3.25 "	110	0.0018	61110
3.30 "	110	0.0015	73333
3.40 "	110	0.0013	84615
3.50 "	110	0.0012	91668
4.00 "	110	0.0011	100000
4.10 "	110	0.0011	100000
4.20 "	110	0.0011	100000
4.30 "	110	0.0011	100000
4.40 "	110	0.0011	100000
4.50 "	110	0.0011	100000
5.00 "	110	0.0011	100000

Manometer No. 3 was used after the fifth filling.

Number of calibration units of air = 401.94.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of a liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.30 P. M., April 25.

The initial pressure, uncorrected, was 5.38 atmospheres.

Table IX.—*Record of Observations.*

(Experiment II. with 0.20 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressures found and calculat'd.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 25, 1905. 8.45 P. M.	458.34	544.38	22°.2	21°.7	0.50	5.50						
April 26. 9.00 A. M.	458.48	539.59	21°.22	20°.22	Atmosphere.	5.81 Atmospheric pressure not deducted.	75.93	Insufficient for quantitative determination.	4.79	4.84	—0.05	346.1
12.00 M.	458.31	539.45	20°.9	20°.2		5.81	75.93		4.79	4.84	—0.05	345.9
3.00 P. M.	458.13	538.91	20°.8	20°.5		5.83	75.53		4.82	4.84	—0.02	342.6
5.00 "	458.36	538.62	20°.82	20°.82		5.87	74.99		4.86	4.84	0.02	340.8
8.30 "	458.46	538.25	20°.9	21°.0		5.90	74.50		4.89	4.84	0.05	338.9
April 27. 9.00 A. M.	458.33	538.45	20°.8	20°.5		5.88	75.12		4.85	4.84	0.01	341.5
												342.6

0.25 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 85.55 grams.

Specific gravity of the solution at 20° = 1.03120.

Grams of sugar in 1,000 cc. at 20° = 81.271.

Concentration of the solution according to the *volume-normal* standard = 0.23748.

Cell A was used. It had been previously set up with a 0.5 weight-normal solution. It was soaked one-half day in distilled water, then subjected to the membrane-forming process, March 16.

Record.

March 16, 1905.

Time.	Voltage.	Current.	Resistance.
3.00 P. M.	114.0	0.0024	47500
3.15 "	113.2	0.0014	80860
3.25 "	112.5	0.0012	93750
3.50 "	112.5	0.0011	102270
4.20 "	112.0	0.0010	112000
4.45 "	111.5	0.0010	111500

Manometer No. 3 was used after the second filling.

Number of calibration units of air—reduced to standard conditions = 380.08.

The cell was set up at 5.00 P. M., March 16, 1905. The solution contained 0.0846 gram $K_4Fe(CN)_6.3H_2O$ per 100 grams of H_2O and the water without contained 0.12488 gram $CuSO_4.5H_2O$ per 100 grams of H_2O.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The initial pressure, uncorrected, was 3.7 atmospheres.

A mistake of 0.1 atmosphere, in the measurement of the osmotic pressure of a 0.25 weight-normal solution, produces an error of 5.67 units in the estimated molecular weight of cane-sugar.

Table X.—Record of Observations.

(Experiment I. with 0.25 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 16, 1905.						Atmospheric pressure not deducted.		Insufficient for quantitative determination.				
5.30 P. M.	402.9	517.8				3.92						
5.45 "	402.9	504.1				4.13						
8.30 "	402.65	472.65	23°.2	23°.75		6.24						
March 17.												
8.45 A. M.	402.7	465.6	22°.4	22°.45	0.53 Atmosphere.	6.91	58.37		6.04	6.08	—0.04	344.7
12.00 M.	402.5	464.6	23°.0	23°.53		6.99	57.41		6.15	6.09	0.06	339.2
2.45 P. M.	402.3	464.1	23°.75	24°.35		7.02	56.80		6.22	6.11	0.11	336.2
5.00 "	402.4	464.7	23°.90	24°.26		6.97	57.46		6.14	6.11	0.03	340.9
8.15 "	402.2	464.7	24°.2	24°.33		6.95	57.64		6.12	6.12	0.00	342.2
												340.6

0.25 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 85.555 grams.

Specific gravity of solution at 20° = 1.03124.

Grams of sugar in 1,000 cc. at 20° = 81.271.

Concentration of the solution according to the *volume-normal* standard = 0.23748.

After experiment No. 1 with a 0.25 weight-normal solution, cell A was soaked in distilled water till 2.55 P. M., March 18. It was then subjected to the membrane-forming process.

Record.

March 18, 1905.

Time.	Voltage.	Current.	Resistance.
3.05 P. M.	110.0	0.0022	50000
3.25 "	110.0	0.0016	68750
3.45 "	110.1	0.0165	6673
4.00 "	110.3	0.0017	64880
4.15 "	110.3	0.0017	64880

The cell was set up at 5.20 P. M., March 18, with a 0.25 weight-normal solution containing the usual amount of potassium ferrocyanide.

The initial pressure, uncorrected, was 2.9 atmospheres.

Manometer No. 3 was used.

Number of calibration units of air, reduced to standard conditions = 380.08.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

0.30 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 102.666 grams.

Specific gravity of solution at 20° = 1.03712.

Grams of sugar in 1,000 cc. at 20° = 96.563.

Concentration of the solution according to the *volume-normal* standard = 0.28213.

Cell A was used. It had previously been used in Experi-

Table XI.—Record of Observations.

(Experiment II. with 0.25 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 18, 1905.												
5.45 P. M.	400.1	542.7				3.18 Atmospheric pressure not deducted.		Insufficient for quantitative determination.				
8.45 "	398.9	474.7	24°.0	23°.97		5.79						
March 19.												
9.45 A. M.	398.5	463.3	21°.9	21°.60	0.53 Atmosphere.	6.75						
12.00 M.	398.8	463.3	21°.75	21°.45		6.71						
1.00 P. M.	398.75	462.14	21°.75	21°.55		6.86	59.00		5.97	6.08	—0.11	348.5
4.00 "	398.78	462.32	21°.90	21°.95		6.84	59.05		5.96	6.07	—0.11	348.7
March 20.												
8.30 A. M.	398.77	462.60	20°.9	20°.65		6.81	59.59		5.92	6.05	—0.13	349.9
12.15 P. M.	398.86	461.45	21°.35	21°.41		6.94	58.28		6.05	6.06	—0.01	342.9
5.20 "	398.60	461.62	21°.4	21°.25		6.89	58.71		6.00	6.06	—0.06	345.8
												347.2

ment II. with a 0.05 weight-normal solution. At the close of this experiment the cell was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

April 3, 1905.

Time.	Voltage.	Current.	Resistance.
10.30 A. M.	110.0	0.0100	11000
10.40 "	110.0	0.0013	84615
11.00 "	110.0	0.0010	110000
11.20 "	110.0	0.0010	110000
11.25 "	110.2	0.0010	110200
11.40 "	110.2	0.0010	110200

The cell was not set up immediately, but was soaked over night in distilled water and again subjected to the membrane-forming process on the following day.

Record.

April 4, 1905.

Time.	Voltage.	Current.	Resistance.
9.20 A. M.	111.2	0.0012	92670
9.30 "	111.5	0.0011	101360
9.50 "	111.6	0.0009	124000
10.00 "	111.6	0.0009	124000
10.10 "	107.0	0.0009	118900
10.20 "	106.5	0.0009	118330
10.30 "	106.5	0.0009	118330
10.40 "	111.0	0.0009	123330
10.50 "	111.0	0.0009	123330

Manometer No. 4 was used.

Number of calibration units reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 11.15 A. M., April 4.

The initial pressure, uncorrected, was 3.15 atmospheres.

Table XII.—Record of Observations.

(Experiment I. with 0.30 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 = 0.0824t)}{P}$.
April 4, 1905.						Atmospheric pressure not deducted.		Insufficient for quantitative determination.				
12.10 P. M.	470.90	599.70				3.75						
3.15 "	468.50	535.10	19°.90	20°.05		6.93						
5.15 "	468.50	528.00	19°.90	20°.15		7.54						
8.30 "	468.10	523.45	19°.92	20°.14		8.25						
April 5.												
9.00 A. M.	468.10	521.60	19°.43	18°.62	0.47 Atmosphere.	8.54	52.10		7.19	7.22	—0.03	343.9
12.00 M.	468.00	521.40	19°.40	19°.46		8.56	51.87		7.23	7.22	0.01	342.0
3.00 P. M.	468.23	520.80	19°.70	20°.65		8.63	50.87		7.38	7.23	0.15	335.4
5.30 "	468.15	520.60	19°.94	20°.60		8.68	50.76		7.20	7.24	—0.04	344.1
April 6.												
8.45 A. M.	468.17	521.45	18°.70	17°.22		8.56	52.16		7.19	7.21	—0.02	343.1
12.00 M.	468.00	521.47	18°.50	17°.9		8.53	52.21		7.18	7.21	—0.03	343.6
												342.0

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.3 weight-normal solution produces an error of 5.4 units in the estimated molecular weight of cane-sugar.

0.30 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 102.666 grams.

Specific gravity of solution at 20° = 1.03712.

Grams of sugar in 1,000 cc. at 20° = 95.563.

Concentration of the solution according to the *volume-normal* standard = 0.28216.

Cell A was used. After Experiment I., with a 0.30 weight-normal solution, it was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

April 7, 1905.

Time.	Voltage.	Current.	Resistance.
9.45 A. M.	110.2	0.0008	137750
10.00 "	110.2	0.0007	157430
10.10 "	110.2	0.0006	183680
10.20 "	110.3	0.0006	183830
10.30 "	110.4	0.0006	184000
10.40 "	110.4	0.0006	184000
10.50 "	110.4	0.0006	184000
11.00 "	110.4	0.0006	184000

Manometer No. 4 was used.

Number of calibration units of air reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for the weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.10 P. M., April 7.

Initial pressure, uncorrected = 2.3 atmospheres.

Table XIII.—Record of Observations.

(Experiment II. with 0.30 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$
April 7, 1905.												
3.00 P. M.	461.40	560.60				4.72 Atmospheric pressure not deducted.		Insufficient for quantitative determination.				
5.30 "	466.16	533.74	19°.92	20°.50		6.78						
8.45 "	466.37	523.40	19°.80	19°.90	0.47 Atmosphere.	7.97						
April 8.												
8.40 A. M.	466.80	522.30	18°.30	16°.85		8.18						
12.30 P. M.	467.70	521.40	18°.10	17°.90		8.44						
3.15 "	465.24	518.43	18°.30	18°.55		8.52	51.79		7.24	7.20	0.04	340.3
5.00 "	465.38	518.21	18°.40	18°.80		8.57	51.42		7.30	7.20	0.10	337.6
9.00 "	465.38	518.20	18°.42	18°.50		8.58	51.47		7.29	7.20	0.09	338.1
April 9.												
9.40 A. M.	465.22	518.65	17°.05	15°.90		8.48	51.52		7.13	7.17	—0.04	344.0
12.00 M.	465.11	518.48	16°.90	16°.20		8.49	52.42		7.14	7.16	—0.02	343.3
5.00 P. M.	465.42	518.20	16°.82	16°.74		8.58	52.75		7.25	7.15	0.10	338.1
												340.2

0.40 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 136.888 grams.

Specific gravity of the solution at 20° = 1.04846.

Grams of sugar in 1,000 cc. at 20° = 126.28.

Concentration according to the *volume-normal* standard = 0.36886.

Cell B was used. It had previously been set up with a 0.20 weight-normal solution. It was soaked over night in distilled water and subjected to the membrane-forming process.

Record.

April 14, 1905.

Time.	Voltage.	Current.	Resistance.
9.30 A. M.	110.0	0.0030	36667
9.50 "	110.3	0.0023	47957
10.00 "	110.0	0.0022	56000
10.20 "	110.4	0.0023	48000
10.30 "	110.4	0.0023	48000
10.40 "	110.3	0.0023	47957
10.50 "	110.3	0.0024	45960
11.00 "	110.3	0.0025	44130
11.10 "	110.2	0.0026	42385
11.20 "	110.2	0.0027	40816
11.30 "	110.2	0.0027	40816

Manometer No. 3 was used.

Number of calibration units of air = 399.05.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.00 M., April 14, with a 0.40 weight-normal solution containing the usual quantity of ferrocyanide.

Initial pressure = 7.21 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.4 weight-normal solution produces an error of 3.8 units in the estimated molecular weight of cane-sugar.

Table XIV.—Record of Observations.

(Experiment I. with 0.40 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 14, 1905.						Atmospheric pressure not deducted.		Insufficient for quantitative determination.				
3.00 P. M.	458.73	504.13	19°.4	19°.25		10.09						
5.00 "	458.80	503.00	19°.4	19°.41		10.37						
8.30 "	458.60	502.50	19°.45	19°.64		10.43						
April 15.												
9.00 A. M.	458.42	501.60	18°.85	18°.50	0.54 Atmosphere.	10.55						
12.30 P. M.	458.77	501.56	18°.70	18°.60		10.63	40.23		9.45	9.61	—0.16	348.1
3.00 "	458.65	501.37	18°.83	19°.34		10.65	40.07		9.49	9.61	—0.12	346.8
5.00 "	458.58	501.23	18°.90	19°.60		10.67	39.97		9.52	9.62	—0.10	345.7
8.00 "	458.58	501.12	19°.10	19°.64		10.70	39.61		9.61	9.62	—0.01	342.7
												345.8

0.40 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 136.888 grams.

Specific gravity of the solution at 20° = 1.04846.

Grams of sugar in 1,000 cc. at 20° = 126.28.

Concentration of the solution according to the *volume-normal* standard = 0.36886.

Cell A was used. It had been previously used in Experiment II., with a 0.20 weight-normal solution. It was soaked in distilled water from 9 A. M. till 11 A. M., April 25, and then subjected to the membrane-forming process.

Record.

April 25, 1905.

Time.	Voltage.	Current.	Resistance.
11.08 A. M.	111.0	0.0020	55500
11.10 "	111.0	0.0015	74000
11.20 "	107.2	0.0012	89330
11.30 "	105.3	0.0011	95730
11.40 "	105.3	0.0011	95730
11.50 "	105.3	0.0011	95730
12.00 M.	105.2	0.0011	95640
12.10 P. M.	105.2	0.0011	95640

Manometer No. 4 was used after the first filling.

Number of calibration units of air = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.30 P. M., April 27, with a 0.40 weight-normal solution containing 0.0846 gram $K_4Fe(CN)_6 \cdot 3H_2O$ per 100 grams of water.

Initial pressure = 3.59 atmospheres.

0.50 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 171.11 grams.

Specific gravity of solution at 20° = 1.05939.

Grams of sugar in 1,000 cc. at 20° = 154.78.

Table XV.—Record of Observations.

(Experiment II. with 0.40 weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 27, 1905.												
4.00 P. M.	476.77	530.50				8.45 Atmospheric pressure not deducted.		Insufficient for quantitative determination.				
5.30 "	476.77	524.60	21°.9	21°.6		9.47						
9.00 "	476.75	519.46	21°.85	21°.7		10.51						
April 28.												
9.00 A. M.	476.81	517.57	21°.2	20°.5	0.49 Atmosphere.	10.99	39.42		9.70	9.69	0.01	342.0
12.30 P. M.	476.75	517.60	20°.9	20°.25		10.98	39.57		9.66	9.68	—0.02	343.1
3.00 "	476.79	517.46	20°.84	20°.4		11.02	39.32		9.73	9.68	0.05	340.5
5.00 "	476.90	517.35	20°.8	20°.54		11.08	39.14		9.78	9.68	0.10	338.8
												341.1

Concentration of the solution according to the *volume-normal* standard = 0.45228.

Cell B was used. It had previously been used with an 0.80 weight-normal solution. After soaking in distilled water for several hours it was subjected to the membrane-forming process.

Record.

April 25, 1905.

Time.	Voltage.	Current.	Resistance.
9.40 A. M.	110	0.0035	31430
9.50 "	110	0.0027	40740
10.00 "	110	0.0023	47825
10.10 "	110	0.0026	42310
10.20 "	110	0.0033	33333
10.30 "	110	0.0038	28956

The cell at this point was again placed in distilled water until 11.15 A. M., when the deposition of the membrane was resumed.

Record.

Time.	Voltage.	Current.	Resistance.
11.25 A. M.	110	0.0038	28950
11.30 "	110	0.0033	33333
11.40 "	110	0.0032	34375
11.45 "	110	0.0032	34375
11.50 "	110	0.0031	35485
12.00 M.	110	0.0031	35485
12.10 P. M.	110	0.0030	36665
12.20 "	110	0.0030	36665
12.30 "	110	0.0030	36665

Manometer No. 4 was used after the first filling.

Number of calibration units of air = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for 1 gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M. with a 0.50 weight-normal solution containing the usual quantity of ferrocyanide.

Table XVI.—Record of Observations.

(Experiment I. with a 0.50 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 25, 1905.												
5.45 P. M.	478.8	514.35	21°.6	21°.5		12.53 Atmospheric pressure not deducted.		Insufficient for quantitative determination.				
8.45 "	478.78	512.91	21°.6	21°.7		13.03						
April 26.												
9.00 A. M.	478.83	512.17	20°.9	20°.3	0.50 Atmosphere.	13.35	32.27		11.98	12.10	—0.12	345.8
12.00 M.	478.78	512.10	20°.8	20°.4		13.35	32.24		11.99	12.10	—0.11	345.4
3.00 P. M.	478.80	512.07	20°.78	20°.7		13.37	32.16		12.00	12.10	—0.10	345.0
5.00 "	478.83	512.05	20°.80	21°.0		13.39	32.08		12.05	12.10	—0.05	343.7
8.30 "	478.76	512.00	20°.94	21°.15		13.38	32.08		12.05	12.10	—0.05	343.7
April 27.												
9.00 A. M.	478.63	511.75	20°.80	20°.62		13.40	32.02		12.07	12.10	—0.03	343.1
												344.5

Initial pressure = 10.33 atmospheres.

A mistake of 0.1 atmosphere, in the measurement of the osmotic pressure of a 0.5 weight-normal solution, produces an error of 3.04 units in the estimated molecular weight of cane-sugar.

0.50 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 171.110 grams.

Specific gravity of the solution at 20° = 1.05938.

Grams of sugar in 1,000 cc. at 20° = 154.78.

Concentration of the solution according to the *volume-normal* standard = 0.45228.

Cell A was used. It had previously been used with a 0.60 weight-normal solution. It was soaked over night and then subjected to the membrane-forming process. The circuit was closed at 10.12 A. M., May 5.

Record.

Time.	Voltage.	Current.	Resistance.
10.15 A. M.	110.4	0.0033	33454
10.20 "	110.5	0.0019	58150
10.30 "	110.5	0.0014	79070
10.40 "	110.7	0.0013	85240
10.50 "	110.7	0.0012	92250
11.00 "	110.7	0.0011	100640
11.10 "	110.7	0.0011	100640
11.20 "	110.7	0.0011	100640
11.30 "	110.8	0.0011	100730
11.40 "	110.7	0.0010	110700
11.50 "	110.8	0.0010	110800
12.00 M.	110.8	0.0010	110800

Manometer No. 4 was used.

Number of calibration units of air under normal conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Table XVII.—Record of Observations.

(Experiment II. with 0.50 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 5, 1905.						Atmospheric pressure not deducted.		Invert sugar found = 0.30 gram in 1,000 grams of water. Correction at 20° = 0.02 atmosphere.				
3.00 P. M.	469.80	509.36	20°.60	20°.40		11.31						
5.30 “	469.75	506.31	20°.55	20°.25		12.20						
9.00 “	469.86	503.85	20°.50	20°.35		13.09						
May 6.												
10.00 A. M.	469.78	502.74	20°.10	19°.70	0.50 Atmosphere.	13.49	31.79		12.16	12.07	0.09	339.7
12.30 P. M.	469.78	502.78	20°.04	19°.70		13.48	32.01		12.08	12 07	0.01	342.0
3.00 “	469.70	502.68	20°.02	20°.00		13.48	31.97		12.06	12.07	—0.01	342.5
5.00 “	469.70	502.70	20°.10	20°.20		13.48	31.98		12.09	12.07	0.02	341.7
8.30 “	469.72	502.50	20°.30	20°.70		13.56	31.69		12.20	12.08	0.12	338.9
May 17.												
10.15 A. M.	469.69	502.42	20°.80	21°.05		13.58	31.61		12.22	12.10	0.12	338.9
12.30 P. M.	469.65	502.40	20°.90	21°.38		13.57	31.59		12.22	12.10	0.12	339.0
												340.4

The cell was set up at 12.30 P. M., May 5, with a 0.50 weight-normal solution containing 0.0846 gram of potassium ferrocyanide per 100 grams of water.

Initial pressure $\doteq$ 8.61 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.50 weight-normal solution produces an error of 3.04 units in the estimated molecular weight of cane-sugar.

0.60 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 205.332 grams.

Specific gravity of the solution at 20° = 1.06986.

Grams of sugar in 1,000 cc. at 20° = 182.24.

Concentration of the solution according to the *volume-normal* standard = 0.53252.

Cell A was used. It had previously been used with a 0.40 weight-normal solution. The cell was soaked in distilled water from April 29 till May 1 and then subjected to the membrane-forming process. The circuit was closed at 10.13 A. M., May 1.

Record.

May 1, 1905.

Time.	Voltage.	Current.	Resistance.
10.15 A. M.	110.0	0.0028	39290
10.20 "	110.0	0.0014	78570
10.30 "	110.0	0.0011	100000
10.40 "	110.0	0.0011	100000
10.50 "	110.0	0.0010	110000
11.00 "	110.0	0.0010	110000
11.10 "	110.0	0.009	122222
11.20 "	110.1	0.009	122330
11.30 "	110.1	0.009	122330
11.40 "	110.1	0.009	122330

Manometer No. 4 was used after first filling.

Number of calibration units of air = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

Table XVIII.—*Record of Observations.*

(Experiment I. with 0.60 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 1, 1905.												
3.00 P. M.	472.84	544.12	20°.10	22°.00		6.45						
5.00 "	472.08	528.88	20°.10	20°.25		8.00						
8.30 "	471.00	518.15	20°.10	20°.30		9.56						
May 2.												
8.15 A. M.	469.35	502.80	19°.20	18°.40		13.30						
12.00 M.	469.22	501.60	19°.06	18°.62		13.69						
3.00 P. M.	469.05	500.76	19°.05	19°.10		14.00						
5.00 "	469.10	500.25	19°.16	19°.50		14.24						
8.30 "	469.00	499.65	19°.30	19°.90		14.47						
May 3.												
9.00 A. M.	468.8	498.21	19°.40	19°.50		15.06						
12.30 P. M.	468.65	497.87	19°.60	20°.10		15.16						
3.00 "	468.72	497.82	19°.86	20°.87		15.26						
5.00 "	468.86	497.60	20°.10	21°.30		15.41						
8.30 "	468.75	497.50	20°.50	21°.90		15.40						
May 4.												
9.00 A. M.	468.72	497.10	21°.21	21°.60	0.51 Atm's-phere.	15.60	27.31		14.23	14.54	—0.31	349.7
12.30 P. M.	468.68	497.00	21°.40	22°.32		15.63	27.19		14.30	14.55	—0.25	348.2
3.30 "	468.86	497.05	21°.80	23°.36		15.70	26.98		14.41	14.57	—0.16	346.0
5.00 "	468.70	497.00	21°.10	23°.80		15.64	27.04		14.38	14.58	—0.20	347.1
												347.7

Atmospheric pressure not deducted.

Invert sugar found = 0.333 gram in 1,000 grams of water.
Correction = 0.02 atmosphere.

The cell was set up at 12 M., May 1, with a 0.60 weight-normal solution.

Initial pressure = 3.98 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.60 weight-normal solution produces an error of 2.52 units in the estimated molecular weight of cane-sugar.

0.60 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 205.332 grams.

Specific gravity of the solution at 20° = 1.06985.

Grams of sugar in 1,000 cc. at 20° = 182.24.

Concentration of the solution according to the *volume-normal* standard = 0.53252.

Cell B was used. It had been previously set up with a weight-normal solution, but when a pressure of 19.5 atmospheres was reached the manometer became loose and the cell was taken down, soaked over night and then subjected to the membrane-forming process. The circuit was closed at 10.30 A. M., May 9.

Record.

May 9, 1905.

Time.	Voltage.	Current.	Resistance.
10.33 A. M.	110.6	0.0071	15580
10.40 "	111.0	0.0037	30000
10.50 "	111.0	0.0031	35810
11.00 "	111.0	0.0030	37000
11.10 "	111.0	0.0028	39640
11.20 "	111.0	0.0027	41110
11.30 "	111.0	0.0026	42690
11.40 "	109.0	0.0024	45420
11.50 "	107.3	0.0023	46650
12.00 M.	110.3	0.0026	42430
12.02 P. M.	110.0	0.0028	35830

The circuit was broken at this point and the cell soaked over night in distilled water. On the following day it was again subjected to the membrane-forming process. The circuit was closed at 11.12 A. M.

Record.

May 10, 1905.

Time.	Voltage.	Current.	Resistance.
11.14 A. M.	110.3	0.0070	15760
11.20 "	110.3	0.0044	25070
11.30 "	110.4	0.0036	30660
11.40 "	110.4	0.0032	34500
11.50 "	110.4	0.0031	35620
12.00 M.	110.4	0.0030	36800
12.10 P. M.	110.4	0.0030	36800
12.20 "	110.4	0.0030	36800

Manometer No. 3 was used after the seventh filling.

Number of calibration units of air in the manometer = 342.13.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M., May 10, with a 0.60 weight-normal solution containing 0.0846 gram of $K_4Fe(CN)_6 \cdot 3H_2O$ per 100 grams of H_2O.

Initial pressure = 9.06 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.60 weight-normal solution produces an error of 2.52 units in the estimated molecular weight of cane-sugar.

0.70 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 239.554 grams.

Specific gravity of solution at 20° = 1.07993.

Grams of sugar in 1,000 cc. at 20° = 208.69.

Concentration of the solution according to the *volume-normal* standard = 0.60981.

Cell B was used. It was soaked in distilled water over night and subjected to the membrane-forming process.

Table XIX.—Record of Observations.

(Experiment II. with 0.60 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure	XII. Difference between pressure found and calculated.	XIII. Molecular weights calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 10, 1905.												
3.00 P. M.	487.49	513.73	22°.9	21°.9		14.51 Atmospheric pressure not deducted.		Invert sugar found = 0.800 gram in 1,000 grams of water. Correction at 20° = 0.05 atmosphere.				
5.30 "	487.37	512.80	22°.7	22°.0		14.96						
8.45 "	487.38	512.31	22°.5	22°.0		15.25						
May 11.												
9.30 A. M.	487.35	512.00	21°.6	20°.82		15.41						
1.00 P. M.	487.31	512.11	21°.5	21°.40		15.33						
4.00 "	487.31	512.44	21°.6	22°.00		15.13						
9.30 "	487.26	512.65	21°.9	22°.60		14.98						
May 12.												
9.15 A. M.	487.30	512.44	22°.1	22°.36		15.13						
12.00 M.	487.40	512.50	22°.3	23°.15		15.16						
3.00 P. M.	487.35	512.40	22°.65	24°.20		15.19						
5.00 "	487.35	512.37	23°.00	25°.00		15.20						
8.30 "	487.36	512.33	23°.7	25°.80	0.53 Atmosphere.	15.39	22.84		14.51	14.66	—0.15	345.8
May 13.											—0.19	
9.00 A. M.	487.30	512.00	24°.6	24°.90		15.40	22.75		14.52	14.71		346.7
5.00 P. M.	487.22	511.88	24°.7	25°.05		15.42	22.66		14.37	14.71	—0.34	350.4
9.00 "	487.24	511.95	24°.8	25°.10		15.39	22.75		14.52	14.72	—0.20	346.9
												347.5

Record.

April 20, 1905.

Time.		Voltage.	Current.	Resistance.
9.35	A. M.	110.6	0.0027	40970
9.55	"	111.0	0.0015	74000
10.00	"	111.0	0.0014	79280
10.10	"	111.0	0.0013	85380
10.20	"	111.0	0.0012	92500
10.30	"	111.0	0.0012	92500
10.40	"	111.0	0.0011	109000
10.50	"	110.0	0.0011	100000
11.00	"	110.0	0.0011	100000
11.10	"	110.0	0.0011	100000

Manometer No. 4 was used after the first filling.

Number of calibration units reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 11.40 A. M., April 20, with a 0.70 weight-normal solution containing the usual amount of potassium ferrocyanide.

Initial pressure = 5.08 atmospheres.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.70 weight-normal solution produces an error of 2.18 units in the estimated molecular weight of cane-sugar.

0.70 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 239.554 grams.

Specific gravity of the solution at 20° = 1.07993.

Grams of sugar in 1,000 cc. at 20 = 208.69.

Concentration of the solution according to the *volume-normal* standard = 0.60981.

Cell B was used. It had previously been used with a 0.60 weight-normal solution. It was soaked from 9.30 A. M. to 3.30

Table XX.—Record of Observations.

(Experiment I. with 0.70 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 20, 1905.												
3.00 P. M.	478.0	510.8	19°.83	20°.21		13.56	Atmospheric pressure not deducted.	Invert sugar found = 0.333 gram in 1,000 grams of water. Correction at 20° = 0.02 atmosphere. Applied to last two measurements.				
5.00 "	476.54	506.44	19°.80	20°.3		14.83						
8.30 "	474.70	501.13	19°.9	20°.52		16.75						
April 21.												
9.30 A. M.	473.75	497.48	19°.7	20°.66	0.52 Atmosphere.	18.33	22.92		17.09	16.87	0.22	338.0
12.30 P. M.	473.35	497.69	19°.81	20°.4		18.11	23.53		16.63	16.88	—0.25	347.4
3.00 "	473.22	497.52	20°.1	21°.4		18.13	23.41		16.72	16.90	—0.18	345.9
5.00 "	473.29	497.56	20°.3	21°.36		18.15	23.39		16.73	16.91	—0.18	346.0
8.30 "	473.30	497.59	20°.6	21°.7		18.11	23.38		16.72	16.93	—0.21	346.5
April 22.												
9.00 A. M.	473.35	497.50	20°.3	19°.8		18.24	23.25		16.82	16.91	—0.19	344.1
												344.8

P. M. and then subjected to the membrane-forming process. The circuit was closed at 3.39 P. M., May 15.

Record.

May 15, 1905.

Time.	Voltage.	Current.	Resistance.
3.40 P. M.	115.1	0.0160	5714
3.45 "	114.4	0.0050	22880
3.50 "	113.5	0.0043	26400
4.00 "	111.5	0.0040	27880
4.10 "	111.2	0.0042	26475

The current was interrupted and the cell soaked till May 16. The circuit was closed at 10.30 A. M.

Record.

May 16, 1905.

Time.	Voltage.	Current.	Resistance.
10.40 A. M.	114.7	0.0046	24930
10.45 "	114.4	0.0040	28600
10.50 "	114.3	0.0039	29310
11.00 "	113.9	0.0038	29980
11.10 "	113.6	0.0037	30700
11.20 "	113.4	0.0036	31500
11.30 "	113.0	0.0036	31390
11.40 "	112.8	0.0036	31330

Manometer No. 3 was used after the seventh filling.

Number of calibration units of air under standard conditions = 342.13.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 12.30 P. M., May 16, 1905.

Initial pressure = 14.35 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.70 weight-normal solution produces an error of 2.18 units in the estimated molecular weight of cane-sugar.

Table XXI.—Record af Observations.

(Experiment II., with 0.70 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 16, 1905.												
3.40 P. M.	488.85	510.10	$25^\circ.10$	$24^\circ.70$	0.53 Atmosphere.	17.81	19.54	Invert sugar found = 0.250 gram in 1,000 grams of water. Correction at 20° = 0.02 atmosphere.	17.04	17.19	—0.15	345.2
5.50 "	488.85	510.00	$25^\circ.00$	$24^\circ.96$		17.89	19.43		17.14	17.18	—0.04	343.1
9.15 "	488 76	510.05	$25^\circ.10$	$25^\circ.40$		17.78	19.53		17.05	17.19	—0.14	345.0
May 17.												
9.15 A. M.	488.85	510.08	$25^\circ.00$	$24^\circ.70$		17.82	19.52		17.06	17.18	—0.12	344.7
12.00 M.	488.85	510.08	$24^\circ.80$	$24^\circ.30$		17.82	19.55		17.03	17.17	—0.14	345.1
3.00 P. M.	488.80	510.02	$24^\circ.60$	$24^\circ.05$		17.84	19.55		17.03	17.16	—0.13	344.8
5.00 "	488.77	510.10	$24^\circ.50$	$24^\circ.05$		17.74	19.65		16.94	17.16	—0.22	346.5
9.30 "	488.82	510.07	$24^\circ.25$	$23^\circ.75$		17.81	19.60		16.98	17.14	—0.16	345.4
May 18.												
9.00 A. M.	488.80	510.03	$23^\circ.20$	$22^\circ.40$		17.83	19.67		16.90	17.08	—0.18	345.8
												345.0

0.80 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 273.776 grams.

Specific gravity of the solution at 20° = 1.08960.

Grams of sugar in 1,000 cc. at 20° = 234.17.

Concentration of the solution according to the *volume-normal* standard = 0.68428.

Cell A was used. It had previously been used with a 0.60 weight-normal solution and was soaked in distilled water from 12.00 M. to 3.00 P. M. It was then subjected to the membrane-forming process.

Record.

April 18, 1905.

Time.	Voltage.	Current.	Resistance.
3.05 P. M.	110	0.0025	44000
3.15 "	110	0.0014	78570
3.25 "	110	0.0012	91670
3.35 "	110	0.0011	100000
3.45 "	110	0.0011	100000
3.55 "	110	0.0011	100000
4.05 "	110	0.0011	100000
4.15 "	110	0.0011	100000
4.25 "	110	0.0011	100000
4.35 "	110	0.0011	100000
4.45 "	110	0.0011	100000

Manometer No. 3 was used after the fifth filling.

Number of calibration units reduced to standard conditions = 401.94.

Values Used in the Computations..

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 3.00 P. M., April 18, with an 0.80 weight-normal solution containing 0.0846 gram $K_4Fe(CN)_6 . 3H_2O$ per 100 grams of water.

Initial pressure = 4.28 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of an 0.80 weight-normal solution produces an error of 1.9 units in the estimated molecular weight of cane-sugar.

Table XXII.—Record of Observations.

(Experiment I. with 0.80 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 18, 1905.												
8.15 P. M.	456.33	511.44	19°.6	18°.8		8.35 Atmospheric pressure not deducted.		Invert sugar found = 0.5450 gram in 1,000 grams water. Correction at 20° = 0.04 atmosphere. Applied to last four measurements.				
April 19.												
9.00 A. M.	455.24	477.61	17°.1	15°.74	0.57 Atmosphere.	19.72						
12.00 M.	455.37	477.47	17°.0	16°.58		20.13						
3.00 P. M.	455.36	477.00	17°.57	18°.36		20.50	20.37		19.30	19.15	0.15	339.5
5.00 "	455.38	476.91	17°.90	18°.81		20.60	20.23		19.38	19.17	0.21	338.5
8.30 "	455.23	476.80	18°.08	18°.97		20.56	20.26		19.40	19.18	0.22	338.4
April 20.												
9.00 A. M.	455.00	476.69	17°.50	16°.96		20.45	20.51		19.07	19.14	—0.07	343.5
12.00 M.	455.16	476.70	17°.64	18°.00		20.59	20.31		19.27	19.15	0.12	340.1
3.00 P. M.	455.15	476.58	18°.15	19°.19		20.69	20.12		19.50	19.18	0.32	336.7
5.00 "	455.18	476.59	18°.42	19°.60		20.71	20.09		19.53	19.20	0.33	336.6
												339.0

0.80 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 273.776 grams.

Specific gravity of the solution at 20° = 1.08960.

Grams of sugar in 1,000 cc. at 20° = 234.17.

Concentration of the solution according to the *volume-normal* standard = 0.68428.

Cell B was used. It had been previously used with a 0.70 weight-normal solution. It was soaked in distilled water from 9.00 A. M. till 2.45 P. M. and was then subjected to the membrane-forming process.

Record.

April 22, 1905.

Time.	Voltage.	Current.	Resistance.
2.50 P. M.	110.0	0.0037	29730
3.00 "	110.0	0.0028	39290
3.10 "	110.0	0.0022	50000
3.30 "	110.0	0.0027	40740
3.45 "	110.0	0.0036	30555
4.10 "	110.0	0.0037	29730
4.20 "	110.1	0.0034	32385
4.30 "	110.1	0.0032	34410
4.40 "	110.1	0.0031	35520
4.50 "	110.1	0.0030	36700
5.00 "	110.1	0.0030	36700
5.10 "	110.1	0.0030	36700

Manometer No. 4 was used after first filling.

Number of calibration units of air reduced to standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.45 P. M., April 22, with an 0.80 weight-normal solution containing 0.0846 gram of potassium ferrocyanide per 100 grams of water.

Initial pressure = 3.25 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of an 0.80 weight-normal solution produces an error of 1.9 units in the estimated molecular weight of cane-sugar.

Table XXIII.—Record of Observations.

(Experiment II. with 0.80 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 22, 1905.												
8.30 P. M.	477.15	511.60	22°.7	20°.92		12.92 Atmospheric pressure not deducted.		Invert sugar found = 0.6665 gram in 1,000 grams of water. Correction at 20° = 0.04 atmosphere. Correction applied to last two measurements.				
April 23.												
10.15 A. M.	474.18	495.30	20°.5	19°.16		20.79						
12.00 M.	474.17	495.20	20°.4	19°.40		20.88						
5.00 P. M.	474.18	495.10	20°.2	19°.85	0.52 Atmosphere.	21.02	20.28		19.37	19.32	0.05	341.4
April 24.												
9.00 A. M.	474.08	494.80	19°.2	18°.40		21.18	20.17		19.48	19.25	0.23	338.3
3.00 P. M.	474.10	494.83	19°.34	19°.92		21.23	20.06		19.55	19.25	0.30	337.3
5.00 "	474.10	494.80	19°.50	20°.40		21.21	20.00		19.61	19.27	0.34	336.4
												338.5

0.89101 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 304.92 grams.

Specific gravity of the solution at 20° = 1.09840.

Grams of sugar in 1,000 cc. at 20° = 256.665.

Concentration of the solution according to the *volume-normal* standard = 0.75.

Cell A was employed. It had previously been used with a 0.75 volume-normal solution and was soaked over night. It was then subjected to the membrane-forming process.

Record.

March 8, 1905.

Time.	Voltage.	Current.	Resistance.
9.50 A. M.	110.2	0.0023	47910
9.55 "	110.5	0.0018	61390
10.00 "	110.5	0.0015	73670
10.20 "	110.5	0.0011	100450
10.30 "	110.5	0.0010	110500
10.40 "	110.5	0.0009	122780
10.50 "	110.5	0.0009	122780
11.05 "	110.5	0.0008	138120
11.15 "	110.5	0.0008	138120
11.25 "	110.5	0.0008	138120

Manometer No. 3 was used.

Number of calibration units of air under standard conditions = 383.39.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 11.50 A. M., March 8, with a 0.75 *volume-normal* (= 0.89101 *weight-normal*) solution.

Initial pressure = 8.00 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of an 0.89101 weight-normal solution produces an error of 1.87 units in the estimated molecular weight of cane-sugar.

Table XXIV.—Record of Observations.

(Experiment I. with 0.89101 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
March 8, 1905. 12.40 P. M.	388.25	441.60				8.32 Atmospheric pressure not deducted.		Correction for inversion = 0.04 atmosphere. Applied to last reading only.				
12.50 "	388.25	435.00				9.42						
2.30 "	387.80	413.40				16.76						
2.50 "	387.60	412.20	19°.45	18°.30		17.42						
4.00 "	387.40	409.20	19°.70	20°.55		19.58						
5.00 "	387.40	408.40	19°.82	20°.60		20.30						
5.40 "	387.10	408.00	19°.95	20°.60		20.40						
8.30 "	387.00	407.00	20°.20	20°.20		21.28						
March 9. 8.30 A. M.	386.80	405.80	19°.60	20°.50	0.62 Atmosphere.	22.38	17.74		21.23	21.48	—0.25	346.1
12.15 P. M.	386.80	405.80	19°.60	19°.80		22.38	17.75		21.21	21.48	—0.27	346.5
2.30 "	386.65	405.70	19°.80	20°.25		22.32	17.76		21.20	21.49	—0.29	346.9
5.30 "	386.75	405.75	20°.20	20°.50		22.38	17.70		21.28	21.52	—0.24	346.1
March 10. 8.15 A. M.	386.70	405.70	17°.50	17°.25		22.38	17.89		21.01	21.32	—0.31	347.0
												346.5

0.90 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 307.998 grams.

Specific gravity of the solution at 20° = 1.09892.

Grams of sugar in 1,000 cc. at 20° = 258.75.

Concentration of the solution according to the *volume-normal* standard = 0.75610.

Cell B was employed. It had been used previously with an 0.80 weight-normal solution. It was soaked over night in distilled water and then subjected to the membrane-forming process.

Record.

April 30, 1905.

Time.	Voltage.	Current.	Resistance.
10.15 A. M.	110	0.0053	20755
10.30 "	110	0.0033	33333
10.40 "	110	0.0031	35485
10.45 "	110	0.0030	36670
10.50 "	110	0.0030	36670
11.05 "	110	0.0029	37930
11.15 "	110	0.0030	36670

Manometer No. 3 was used after the sixth filling.

Number of calibration units of air under standard conditions = 368.99.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 when reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M., April 30, with a 0.90 weight-normal solution containing 0.0846 gram $K_4Fe(CN)_6.3H_2O$ per 100 grams of H_2O.

Initial pressure = 14.86 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 0.90 weight-normal solution produces an error of 1.69 units in the estimated molecular weight of cane-sugar.

Table XXV.—Record of Observations.

(Experiment I. with 0.90 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
April 30, 1905.												
8.15 P. M.	467.10	484.9	21°.2	21°.0	0.57 Atmosphere.	22.90 Atmospheric pressure not deducted.	16.58	Invert sugar found = 0.7125 gram in 1,000 grams of water. Correction at 20° = 0.05 atmosphere.	21.82	21.81		342.1
May 1.												
9.30 A. M.	467.00	484.65	20°.2	19°.6		23.09	16.60		21.80	21.74	0.06	341.2
1.30 P. M.	467.00	484.66	20°.1	20°.0		23.08	16.56		21.85	21.73	0.12	340.4
3.00 "	466.98	484.67	20°.1	20°.25		23.03	16.58		21.82	21.73	0.09	340.9
5.00 "	467.06	484.65	20°.1	20°.40		23.16	16.48		21.96	21.73	0.23	338.6
8.30 "	466.97	484.68	20°.1	20°.40		23.01	16.59		21.81	21.73	0.08	341.0
May 2.												
8.45 A. M.	467.00	484.60	19°.26	18°.60		23.15	16.59		21.81	21.67	0.14	340.0
12.00 M.	467.00	484.60	19°.10	18°.90		23.15	16.57		21.84	21.65	0.19	339.3
3.00 P. M.	467.00	484.59	19°.10	19°.30		23.16	16.54		21.82	21.65	0.17	339.6
5.00 "	467 06	484.60	19°.16	19°.70		23.23	16.47		21.91	21.66	0.25	338.3
												340.1

1.00 Weight-Normal Solution—Experiment I.

Sugar dissolved in 1,000 grams of water = 342.22 grams.

Specific gravity of the solution at 20° = 1.10791.

Grams of sugar in 1,000 cc. at 20° = 282.45

Concentration of the solution according to the *volume-normal* standard = 0.82534.

Cell A was employed. It had previously been used with a normal solution which registered 21.7 atmospheres uncorrected pressure when the manometer was dislodged from the cell. It was then soaked over night and subjected to the membrane-forming process. The circuit was closed at 10.37 A. M.

Record.

May 11, 1905.

Time.	Voltage.	Current.	Resistance.
10.40 A. M.	112.0	0.0021	53300
10.45 "	112.0	0.0016	70010
10.55 "	112.0	0.0015	74670
11.00 "	112.0	0.0013	84200
11.10 "	112.0	0.0011	101800
11.20 "	112.0	0.0011	101800
11.30 "	111.9	0.0010	111900
11.40 "	111.8	0.0010	111800
11.50 "	111.8	0.0010	111800
12.00 M.	110.8	0.00095	116600
12.10 P. M.	110.8	0.00095	116600
12.20 "	110.8	0.00095	116600

Manometer No. 4 was used.

Number of calibration units of air under standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 1.00 P. M., May 11.

Initial pressure = 6.26 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a weight-normal solution produces an error of 1.52 units in the estimated molecular weight of cane-sugar.

Table XXVI.—Record of Observations.

(Experiment I. with 1.00 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 11, 1905.												
4.00 P. M.	477.42	504.83	22°.70	21°.30		16.12 Atmospheric pressure not deducted.		Invert sugar found = 0.7245 gram in 1,000 grams of water. Correction at 20° = 0.05 atmosphere.				
9.30 "	476.15	497.57	22°.60	22°.60		20.50						
May 12.												
9.15 A. M.	474.83	492.28	22°.30	22°.26		25.06						
12.00 M.	474.67	491.87	22°.45	22°.97		25.42						
3.00 P. M.	474.48	491.39	22°.82	24°.10		25.84						
5.00 "	474.52	491.27	22°.20	24°.90	0.52 Atmosphere.	26.01	15.95		24.76	24.40	0.36	337.3
8.30 "	474.40	491.10	22°.90	25°.80		26.16	15.86		24.90	24.45	0.45	336.2
May 14.												
11.00 A. M.	474.25	490.85	24°.00	23°.41		26.32	15.88		24.87	24.46	0.41	336.6
1.00 P. M.	474.08	490.81	23°.90	23°.30		26.12	16.01		24.67	24.45	0.22	339.4
5.30 "	474.00	490.81	23°.60	23°.22		26.00	16.09		24.54	24.43	0.11	340.7
												338.04

1.00 Weight-Normal Solution—Experiment II.

Sugar dissolved in 1,000 grams of water = 342.22 grams.

Specific gravity of the solution at 20° = 1.10791.

Grams of sugar in 1,000 cc. at 20° = 282.45.

Concentration of the solution according to the *volume-normal* standard = 0.82534.

Cell A was employed. It had previously been used with a weight-normal solution. It was soaked in distilled water over night and then subjected to the membrane-forming process. The circuit was closed at 3.26 P. M., May 16.

Record.

May 16, 1905.

Time.	Voltage.	Current.	Resistance.
3.30 P. M.	116.5	0.0031	37580
3.35 "	116.0	0.0020	58000
3.40 "	115.7	0.0017	68060
3.50 "	115.0	0.0015	76670
4.00 "	114.6	0.0013	88150
4.10 "	114.3	0.0012	95250
4.20 "	113.9	0.0012	94920
4.30 "	113.7	0.0012	94750
4.40 "	113.4	0.0012	94500
4.50 "	113.3	0.0012	94420

Manometer No. 4 was used.

Number of calibration units of air under standard conditions = 402.66.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.30 P. M., May 16, with a weight-normal solution.

Initial pressure = 11.75 atmospheres, uncorrected.

A mistake of 0.1 atmosphere in the measurement of the osmotic pressure of a 1.00 weight-normal solution produces an error of 1.52 units in the estimated molecular weight of cane-sugar.

Table XXVII.—Record of Observations.

(Experiment II. with 1.00 Weight-Normal Solution.)

I. Time.	II. Top of manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 16, 1905. 9.15 P. M.	475.65	497.72	25°.30	25°.80		19.91 Atmospheric pressure not deducted.		Invert sugar found = 0.665 gram in 1,000 grams of water. Correction at 20° = 0.04 atmosphere.				
May 17. 9.15 A. M.	473.82	491.57	25°.40	24°.70		24.65						
12.00 M.	473.85	491.10	25°.10	24°.35		25.34						
3.00 P. M.	473.57	490.86	24°.95	24°.10		25.29						
5.00 "	473.62	490.67	24°.70	24°.10		25.62						
9.30 "	473.35	490.23	24°.40	23°.75		25.89						
May 18. 9.00 A. M.	473.50	490.60	23°.30	22°.45		23.44						
12.30 P. M.	473.15	491.53	23°.10	22° 70		23.82						
3.00 "	473.10	490.09	23°.65	23°.00		25.73						
5.00 "	473.15	490.86	23°.00	23°.10		24.18						
9.30 "	473.20	490.07	23°.00	23°.10	0.52	25.90	16.17		24.42	24.38	0.04	341.7
May 19. 9.00 A. M.	473.05	489.93	22°.50	22°.10	Atmosphere.	25.89	16.22		24.34	24.34	0.00	342.2
12.00 M.	473.20	489.90	22°.40	22°.30		26.16	16.05		24.61	24.33	0.28	338.4
3.00 P. M.	473.08	489.90	22°.40	22°.55		25.98	16.14		24.46	24.33	0.13	340.5
5.30 "	473.10	489.85	22°.40	22°.70		26.09	16.07		24.57	24.33	0.24	339.0
9.30 "	472.95	489.83	22°.50	22°.80		25.89	16.18		24.40	24.34	0.06	341.4
May 20. 9.30 A. M.	473.00	489.75	21°.90	21°.40		26.08	16.14		24.42	24.29	0.13	340.4
												340.5

1.00 Weight-Normal Solution—Experiment III.

Sugar dissolved in 1,000 grams of water = 342.22 grams.

Specific gravity of the solution at 20° = 1.10791.

Grams of sugar in 1,000 cc. at 20° = 282.45.

Concentration of the solution according to the *volume-normal* standard = 0.82534.

Cell B was employed. It was previously used with a weight-normal solution and afterwards soaked in distilled water from 9.00 A. M. to 3.45 P. M. The circuit was closed at 3.47 P. M.

Record.

May 18, 1905.

Time.	Voltage.	Current.	Resistance.
3.50 P. M.	110.0	0.0075	14640
3.57 "	110.0	0.0056	19640
4 00 "	110.0	0.0043	25580
4.10 "	110.0	0.0038	28290
4.20 "	110.0	0.0034	32360
4.30 "	110.0	0.0032	34380
4.40 "	110.0	0.0032	34380
4.50 "	110.0	0.0032	34380
5.00 "	110.0	0.0031	35480
5.10 "	110.0	0.0031	35480
5.20 "	110.0	0.0038	28950

Manometer No. 3 was used.

Number of calibration units of air under standard conditions = 342.13.

Values Used in the Computations.

0.003665, for temperature coefficient of gases.

0.089826, for weight of 1 liter of H_2 at Baltimore.

22.488, atmospheres pressure for a gram-molecular weight of H_2 reduced, at 0°, to a volume of 1 liter.

The cell was set up at 5.30 P. M., May 18.

Initial pressure, uncorrected = 14.6 atmospheres.

Table XXVIII.—Record of Observations.

(Experiment III. with 1.00 Weight-Normal Solution.)

I. Time.	II. Top of the manometer.	III. Top of mercury column.	IV. Temperature of the solution.	V. Temperature of air in the manometer.	VI. Pressure of liquids in the manometer.	VII. Pressure in atmospheres, uncorrected.	VIII. Calibration units of air in the manometer.	IX. Correction for inversion.	X. Pressure in atmospheres, corrected.	XI. Theoretical gas pressure.	XII. Difference between pressure found and calculated.	XIII. Molecular weight calculated from the equation $M = \frac{W(22.488 + 0.0824t)}{P}$.
May 18, 1905.												
9.30 P. M.	491.30	507.15	23°.30	22°.90		23.69 Atmospheric pressure not deducted.		Correction at 20° = 0.04 atmosphere. Invert sugar found = 0.665 gram in 1,000 grams of water.				
May 19.												
9.00 A. M.	491.20	506.72	22°.50	21°.75		24.26						
12.00 M.	491.15	506.90	22°.35	21°.95		23.85						
3.00 P. M.	491.18	506.55	22°.30	22°.30		24.43						
5.30 "	491.24	506.50	22°.35	22°.50		24.60						
May 20.												
9.30 A. M.	491.15	506.10	21°.90	21°.30	0.54 Atmosphere.	25.06	13.88		24.19	24.29	—0.10	343.7
12.00 M.	491.20	506.10	21°.76	21°.40		25.18	13.82		24.29	24.28	0.01	342.1
3.00 P. M.	491.21	506.00	21°.70	21°.60		25.37	13.71		24.49	24.27	0.22	339.2
5.00 "	491.17	506.07	21°.70	21°.80		25.19	13.81		24.27	24.27	0.00	342.3
9.30 "	491.23	506.00	21°.75	21°.90		25.40	13.68		24.51	24.28	0.23	339.0
May 21.												
12.00 M.	491.20	505.89	20°.80	20°.30		25.84	13.77		24.34	24.20	0.14	340.3
												341.1

Table XXIX.—Summary of Results.

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
Experiment I.					
0.05	1.23	1.21	0.02	336.3	
	1.23	1.21	0.02	336.1	
	1.28	1.21	0.07	323.3	
	1.31	1.21	0.10	316.1	
	1.34	1.21	0.13	309.4	
	1.28	1.21	0.07	323.9	
	1.26	1.21	0.05	327.5	
	1.28	1.21	0.07	323.8	
	1.30	1.22	0.08	319.7	324.0
Experiment II.					
	1.16	1.21	—0.05	357.1	
	1.20	1.21	—0.01	345.1	
	1.26	1.21	0.05	328.7	
	1.29	1.21	0.08	320.3	
	1,27	1.21	0.06	326.1	
	1.29	1.21	0.08	320.9	
	1.28	1.21	0.07	323.5	331.7
Experiment I.					
0.10	2.52	2.41	0.11	327.7	
	2.50	2.41	0.09	330.5	
	2.07	2.37	[—0.30!]	[393.0!]	
	2.22	2.38	—0.11	359.5	
	2.49	2.40	0.09	330.4	337.0
Experiment II.					
	2.36	2.40	—0.04	348.0	
	2.44	2.40	0.04	336.9	
	2.46	2.40	0.06	334.5	
	2.50	2.40	0.10	329.4	
	2.46	2.40	0.06	333.0	
	2.44	2.40	0.04	336.8	336.6

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Differencebetween pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
			Experiment I.		
0.20	4.75	4.85	—0.10	349.8	
	4.75	4.85	—0.10	349.8	
	4.80	4.85	—0.05	345.6	
	4.77	4.83	—0.06	346.4	
	4.75	4.82	—0.07	347.3	
	4.77	4.82	—0.05	345.9	
	4.78	4.82	—0.04	345.2	347.1
			Experiment II.		
	4.79	4.84	—0.05	346.1	
	4.79	4.84	—0.05	345.9	
	4.82	4.84	—0.02	342.6	
	4.86	4.84	0.02	340.8	
	4.89	4.84	0.05	338.9	
	4.04	4.84	0.01	341.5	342.6
			Experiment I.		
0.25	6.04	6.08	—0.04	344.7	
	6.15	6.09	0.06	339.2	
	6.22	6.11	0.11	336.2	
	6.14	6.11	0.03	340.9	
	6.12	6.12	0.00	342.2	340.6
			Experiment II.		
	5.97	6.08	—0.11	348.5	
	5.96	6.07	—0.11	348.7	
	5.92	6.05	—0.13	349.9	
	6.05	6.06	—0.01	342.9	
	6.00	6.06	—0.06	345.8	347.2
			Experiment I.		
0.30	7.19	7.22	—0.03	343.9	
	7.23	7.22	0.01	342.0	
	7.38	7.23	0.15	345.4	
	7.20	7.24	—0.04	344.1	
	7.19	7.21	—0.02	343.1	
	7.18	7.21	—0.03	343.6	342.0

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
Experiment II.					
	7.24	7.20	0.04	340.3	
	7.30	7.20	0.10	339.6	
	7.29	7.20	0.09	338.1	
	7.13	7.17	—0.04	344.0	
	7.14	7.16	—0.02	343.3	
	7.25	7.15	0.10	338.1	340.2
Experiment I.					
0.40	9.45	9.61	—0.16	348.1	
	9.49	9.61	—0.12	346.8	
	9.52	9.62	—0.10	345.7	
	9.61	9.62	—0.01	342.7	345.8
Experiment II.					
	9.70	9.69	0.01	342.0	
	9.66	9.68	—0.02	343.1	
	9.73	9.68	0.05	340.5	
	9.78	9.68	0.10	338.8	341.1
Experiment I.					
0.50	11.98	12.10	—0.12	345.8	
	11.99	12.10	—0.11	345.4	
	12.00	12.10	—0.10	345.0	
	12.05	12.10	—0.05	343.7	
	12.05	12.10	—0.05	343.7	
	12.07	12.10	—0.03	343.1	344.5
Experiment II.					
	12.16	12.07	0.09	339.7	
	12.08	12.07	0.01	342.0	
	12.06	12.07	—0.01	342.5	
	12.09	12.07	0.02	341.7	
	12.20	12.08	0.12	338.9	
	12.22	12.10	0.12	338.9	
	12.22	12.10	0.12	339.0	340.4
Experiment I.					
0.60	14.23	14.54	—0.31	349.7	
	14.30	14.55	—0.25	348.2	
	14.41	14.57	—0.16	346.0	
	14.38	14.58	—0.20	347.1	347.7

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
		Experiment II.			
	14.51	14.66	—0.15	345.8	
	14.52	14.71	—0.19	346.7	
	14.37	14.71	—0.34	350.4	
	14.52	14.72	—0.20	346.9	347.5
		Experiment I.			
0.70	17.09	16.87	0.22	338.0	
	16.63	16.88	—0.25	347.4	
	16.72	16.90	—0.18	345.9	
	16.73	16.91	—0.18	346.0	
	16.72	16.93	—0.21	346.5	
	16.82	16.91	—0.19	344.1	344.7
		Experiment II.			
	17.04	17.19	—0.15	345.2	
	17.14	17.18	—0.04	343.1	
	17.05	17.19	—0.14	345.0	
	17.06	17.18	—0.12	344.9	
	17.03	17.17	—0.14	345.1	
	17.03	17.16	—0.13	344.8	
	16.94	17.16	—0.22	346.5	
	16.98	17.14	—0.16	345.4	
	16.90	17.08	—0.18	345.8	345.0
		Experiment I.			
0.80	19.30	19.15	0.15	339.5	
	19.38	19.17	0.21	338.5	
	19.40	19.18	0.22	338.4	
	19.07	19.14	—0.07	343.5	
	19.27	19.15	0.12	340.1	
	19.50	19.18	0.32	336.7	
	19.53	19.20	0.33	336.6	339.0
		Experiment II.			
	19.37	19.32	0.05	341.4	
	19.48	19.25	0.23	338.3	
	19.55	19.25	0.30	337.3	
	19.61	19.37	0.34	336.4	338.5

Weight-normal concentration of solution.	Osmotic pressure, observed. (Atmospheres.)	Gas pressure calculated for same temperature. (Atmospheres.)	Difference between pressure observed and calculated.	Molecular weight calculated from observed pressure.	Molecular weights. Mean values.
0.89101	21.23	21.48	—0.25	346.1	
	21.21	21.48	—0.27	346.5	
	21.20	21.49	—0.29	346.9	
	21.28	21.52	—0.24	346.1	
	21.08	21.32	—0.31	347.0	346.5
0.90	21.82	21.81	0.01	342.1	
	21.80	21.74	0.06	340.4	
	21.85	21.73	0.12	340.9	
	21.82	21.73	0.09	338.6	
	21.96	21.73	0.23	341.0	
	21.81	21.73	0.08	340.0	
	21.81	21.67	0.14	339.3	
	21.84	21.65	0.19	339.6	
	21.82	21.65	0.17	338.3	
	21.91	21.66	0.25	338.3	340.1
Experiment I.					
1.00	24.76	24.40	0.36	337.3	
	24.90	24.45	0.45	336.2	
	24.87	24.46	0.41	336.6	
	24.67	24.45	0.22	339.4	
	24.54	24.43	0.11	340.7	
	24.79	24.39	0.40	336.7	337.8
Experiment II.					
	24.42	24.38	0.04	341.7	
	24.34	24.34	0.00	342.2	
	24.61	24.33	0.28	338.4	
	24.46	24.33	0.13	340.5	
	24.57	24.33	0.24	339.0	
	24.40	24.34	0.06	341.4	
	24.42	24.29	0.13	340.4	340.5
Experiment III.					
	24.19	24.29	—0.10	343.7	
	24.29	24.28	0.01	342.1	
	24.49	24.27	0.22	339.2	
	24.27	24.27	0.00	342.3	
	24.51	24.28	0.23	339.0	
	24.34	24.20	0.14	340.3	341.1

Table XXX.—Mean Molecular Weight for each Concentration.

Concentration.	Molecular weight.
0.05	327.9
0.10	336.8
0.20	344.9
0.25	343.9
0.30	341.1
0.40	343.5
0.50	340.4
0.60	347.7
0.70	344.8
0.80	338.8
0.89101	346.5
0.90	340.1
1.00	339.8
Mean of all determinations,	341.2

It may be questioned whether the pressures which we have measured were *maximum* pressures ; whether, in other words, the solutions would not, later, have developed still higher pressures if an opportunity had been given them to do so. We have tested this point on several occasions by allowing cells to remain up from one to two weeks after pressures, such as we have recorded, had been developed and have observed, in all cases, a very slight increase from day to day, but this never exceeded the increase of pressure which was to be expected from the progress of the inversion of the sugar.

The results recorded in this communication appear to the authors to make it probable that the determining factor in osmotic pressure is the numerical ratio existing between the molecules of the dissolved substance and of the solvent, rather than the number of molecules of the dissolved substance which are contained in a unit volume of the solution ; further, that the hypothesis of van't Hoff holds good provided we consider, as the standard quantity of the solvent, that mass of pure water which has the *gas-unit* volume, *i. e.*, 1 liter, at the temperature of maximum density. The results are, perhaps, as concordant as could be expected from a first series of measurements in a field where the progress of the work is hampered by considerable experimental difficulties, but they are by no means the most precise which can be obtained. Certain sources of error which have, up to the present, beset the work and lessened the precision of the results, can be either altogether eliminated or brought under much better control than hitherto. The measurement of the osmotic pressure of cane-sugar solutions will, therefore, be repeated at an early date, and an attempt will then be made to improve the procedure in various ways, with a view to testing more thoroughly the inferences drawn from the results of the previous work

The sources of error to which particular attention will be given in the future are: (1) The *thermometer effects*, (2) the uncertainty regarding the true volume of the upper end of the manometer, and (3) the inversion which takes place in the cell.

The source of error which, from the beginning of the work to the end, has given us the most concern is the thermometer effects, *i. e.*, the temporary fluctuations of pressure which follow changes of temperatures, and are due to the expansion or contraction of the liquids in the cell, rather than to actual variations in osmotic pressure. These effects can, of course, be eliminated by maintaining the cell at a constant temperature, or by reducing the rate of change of temperature to a point where the passage of water through the membrane and its distribution through the solution can keep pace with the fluctuations of temperature. We attempted to realize the latter condition by surrounding the cell wlth non-conducting material, but our efforts were not wholly successful, and we were well aware of the fact that many of the apparent variations in osmotic pressure were, in reality, due to thermometer effects. In the future we shall attempt to maintain constant temperature.

The uncertainty regarding the true volume of that portion of the manometer whose form is affected by the sealing of the instrument does not seriously affect the measurement of the pressure of dilute solutions, but it becomes a matter of great importance when the pressure of a concentrated solution is to be determined.

We are inclined to believe that the inversion of the cane-sugar in the more concentrated solutions was greater than it was, apparently, found to be by the method which was employed to determine it, and when the work is repeated, the polariscope, instead of Fehling's solution, will be used to measure the inversion which has taken place in the cell.

In his book on Solutions, Ostwald says: "*Dissolved substances exert the same pressure, in the form of osmotic pressure, as they would exert were they gasified, at the same temperature, without change of volume.*" This statement fairly represents, we think, the view generally held respecting the proper magnitude of osmotic pressure, and the known deviations from the rule, as given above, have been regarded as abnormalities, to be reconciled in some way, not yet clear, with the supposed law. The results which we have obtained in the measurement of the osmotic pressure of cane-sugar solutions may be summarized in the following words: *Cane-sugar, dissolved in water, exerts an osmotic pressure equal to that which it would exert if it were gasified at the same temperature and the volume of the gas were reduced to that of the solvent in the pure state.* In other words, dissolved cane-sugar exerts an osmotic pressure throughout the *larger volume of the solution equal to that which, as a gas, it would exert if confined to the smaller volume of the pure solvent.* Stated in this way, all of the thirteen concentrations which have been tested conform to the rule, and no abnormalities appear. Whether the correct standard is the volume of the solvent at the temperature of maximum density, or at the temperature at which the osmotic pressure is measured, will have to be determined by future investigation. The margin of experimental error is still too great to enable us to discriminate between these two possible magnitudes.

The recognition of the fact that the volume relations of solvent and solution play such an important part in the osmotic pressure of cane-sugar solutions led to the suggestion that the so-called *abnormal* freezing-points of the higher concentrations of the same solutions may, in some way, be dependent on, or related to, the degree of the distension of the solvent by the dissolved matter. Accordingly we determined the freezing-points and the density, at zero or slightly below, of all except two of the concentrations, the osmotic pressure of which had been measured. This work is of such recent date that we have not yet been able to develop, except in a superficial manner, the relations which were found to hold between osmotic pressure on the one side and the depressions of the freezing-point on the other. It is, however, already clear that, in the solution of the problem of *abnormal* freezing-points, some assistance may be expected from a consideration of the relative weights of equal volumes of solvent and solution.

Some of the relations which have appeared will be pointed out :

Let N = the concentration of the solution according to the *weight-normal* standard, *i. e.*, the proportion of a gram-molecular weight of sugar which is dissolved in 1,000 grams of water.

Let D = the density of the solution at its freezing-point, *i.e.*, the relative weights of equal volumes of solution and pure solvent near the temperature of freezing.

Let Δ = the observed depression of the freezing-point.

Let Δ_1 = the calculated depression of the freezing-point.

Then $\Delta_1 = 1.85\ N\ D$ *for all concentrations.*

The verification of the rule will be found in Table XXXI. It will be seen that the observed and calculated depressions of the freezing-points are in close accord for every concentration except possibly two—the 0.50 and 1.00 weight-normal solutions, in which the deviations amount to 0°.011 and 0°.022, respectively. Whether these discrepancies are real, or only the result of experimental errors, we have not yet had time to ascertain The fact, however, that the concentrations on either side of those in question show close conformity to the rule suggests the latter explanation.

The last solution given in the table (the 1.26806 *weight-normal* one) is a *volume-normal* solution, *i. e.*, a solution containing a gram-molecular weight of sugar in a liter volume. The depression of the freezing-point of this solution has been regarded as *abnormal* by the difference between 1°.85 and 2°.66, but it will be noticed that it conforms to the rule with the same degree of precision as the 0.1 weight-normal solution.

Table XXXI.

N.	D.	Δ_1. (1.85 N. D.)	Δ.
0.10	1.0129	0°.187	0°.187
0.20	1.0257	0°.379	0°.373
0.30	1.0380	0°.576	0°.574
0.40	1.0497	0°.777	0°.776
0.50	1.0611	0°.981	0°.970
0.60	1.0717	1°.189	1°.187
0.70	1.0825	1°.401	1°.398
0.80	1.0918	1°.616	1°.612
0.90	1.1016	1°.834	1°.837
1.00	1.1110	2°.060	2°.082
1.26806	1.1340	2°.660	2°.660

A somewhat different aspect of the problem is presented when we consider the apparent influence of the density of the solution upon the equivalence of the freezing-point lowering to osmotic pressure at the temperature of freezing.

If we divide the observed depression of the freezing-point of each weight-normal concentration of solution by the theoretical gas (osmotic) pressure at 0° of the dissolved sugar, we obtain a series of numbers which differ considerably among themselves. This is shown in Table XXXII., in which the weight-normal concentrations of the various solutions occupy the first column, the observed depressions of the freezing-points the second, and the corresponding theoretical gas or osmotic pressures the third. The quotients referred to are given in the fourth column. They are quite irregular in value, but if we divide each of them by the density of the solution near the freezing-point (column 5), we obtain a nearly constant value (column 6), which can be utilized to calculate either osmotic pressure or freezing-point lowering. The mean of all the values so obtained is 0.082.

Table XXXII.

Weight-normal concentration of the solution.	Observed lowering of the freezing-point.	Theoretical gas pressure at 0°.	Observed lowering of the freezing-point divided by the theoretical gas pressure.	Density of the solution at the freezing-point.	Observed lowering of the freezing-point divided by the theoretical gas pressure × density.
0.1	0°.187	2.2488	0.0831	1.0129	0.0818
0.2	0°.373	4.4976	0.0829	1.0257	0.0808
0.3	0°.574	6.7464	0.0895	1.0380	0.0818
0 4	0°.776	8.9952	0.0865	1.0497	0.0821
0.5	0°.969	11.244	0.0862	1.0611	0.0814
0.6	1°.187	13.4928	0.0879	1.0717	0.0820
0.7	1°.398	15.7416	0.0888	1.0825	0.0818
0.8	1°.612	17.9904	0.0896	1.0918	0.0818
0.9	1°.837	20.2392	0.0907	1.1016	0.0828
1.0	2°.082	22.488	0.0926	1.1110	0.0831
1.26806	2°.660	28.765	0.0924	1.1340	0.0822
				Mean value,	0.082

Let D = the density—as compared with water at 0°—of any weight-normal cane-sugar solution near its freezing-point.

Let Δ = the observed lowering of its freezing-point.

Let P = the theoretical osmotic pressure of the solution at 0°.

Then with the aid of the equation $\frac{\Delta}{PD} = 0.082$ it is possible to calculate, very closely, either the osmotic pressure or the depression of the freezing-point of any solution when the other values are known. If the osmotic pressure is known, the depression of the freezing-point will be found by the equation $\Delta = 0.082 \times P \times D$. Or, if the depression of the freezing-point of a cane-sugar solution is known, the osmotic pressure of the solution, at 0°, can be calculated by the equation $P = \frac{\Delta}{0.082 \times D}$. The verification of these equations will be found in Tables XXXIII. and XXXIV.

Table XXXIII.

Concentration.	Osmotic pressure at 0°.	Density of solution at its freezing-point.	Observed lowering of freezing-point.	Osmotic pressure at 0° × density × 0.082.
0.1	2.25	1.0129	0°.187	0.187
0.2	4.50	1.0257	0°.373	0.378
0.3	6.75	1.0380	0°.574	0.574
0.4	9.00	1.0497	0°.776	0.774
0.5	11.24	1.0611	0°.969	0.978
0.6	13.49	1.0717	1°.187	1.185
0.7	15.74	1.0825	1°.398	1.397
0.8	17.99	1.0918	1°.612	1.610
0.9	20.24	1.1016	1°.837	1.828
1.0	22.49	1.1110	2°.082	2.049
1.26806	28.76	1.1340	2°.660	2.674

Table XXXIV.

Concentration.	Observed lowering of freezing-point.	Density of solutions at the freezing-point.	Theoretical gas or osmotic pressure at 0°.	Values of $\frac{\Delta}{0.082D}$ *i. e.*, calculated osmotic pressures.
0.1	0°.187	1.0129	2.25	2.25
0.2	0°.373	1.0257	4.50	4.43
0.3	0°.574	1.0380	6.75	6.74
0.4	0°.776	1.0497	9.00	9.01
0.5	0°.969	1.0611	11.24	11.13
0.6	1°.187	1.0717	13.49	13.50
0.7	1°.398	1.0825	15.74	15.75
0.8	1°.612	1.0918	17.99	18.00
0.9	1°.837	1.1016	20.24	20.33
1.0	2°.082	1.1110	22.49	22.85
1.26806	2°.660	1.1340	28.76	28.82

The conformity to the rule as stated is, in some cases, not as close as could be desired, but the experimental data from which the rule was deduced were gathered rather hastily and have not yet been carefully scrutinized. It is, nevertheless, obvious that the relations here pointed out should be taken into consideration in any attempt to solve the problem of the so-called *abnormal* depressions of the freezing-point. To us it seems probable that at least some of the abnormalities will disappear when the problem is studied from the side of the volume relations of solution and pure solvent; in other words, that, as in the case of osmotic pressure, all concentrations of solution will be found to conform to general rules.

New Semi-Permeable Membranes.

It was stated by one of us, in a preliminary communication,[1] that the electrolytic process is adapted to the deposition, upon or within porous walls, of nearly every kind of precipitate which can be formed from electrolytes in solution and that we were, therefore, in a position to test a variety of insoluble or slightly soluble substances with respect to their possession of the semi-permeable character.

The following substances have thus far been found to exhibit decided osmotic activity, and some of them to a degree which promises future usefulness in the measurement of pressure :

Aluminium hydroxide
Ferric "
Ferric phosphate
Uranyl "
Cupric "
Uranyl ferrocyanide
Stannous "
Cadmium "
Zinc "
Nickel "

Cobalt cobalticyanide
Nickel "
Ferrous "
Copper "
Zinc "
Cadmium "
Manganese "

The compounds mentioned above, as well as several others which appeared to be less promising, were investigated in this laboratory by Messrs. Carver, Coony, and Hall.

Unfortunately, however, the only porous vessels which were available for their work were bottle-shaped cells of 200 cc. capacity, the walls of which were of such open texture and so full of " air blisters" that quantitative measurements of pressure were impossible. They were, therefore, obliged to limit their investigation of these membranes to a determination of the quantities of water which would pass through them in a given time when the cells, filled with solutions of definite concentration, were placed in water ; but the activity of osmotic cells in this respect is determined, very largely, by the texture of the cell wall, hence no very definite conclusions could be drawn with regard to the suitability of any of the substances for the quantitative measurement of pressure. Since we have had at our disposal a few cells of excellent character for quantitative work, the investigation of these membranes has been resumed, and each one of them will now be tested by actual use in the measurement of pressure.

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[1] THIS JOURNAL, **29**, 173.

JOHNS HOPKINS UNIVERSITY,
May 25, 1905.

REPORT.

A Revision of the Atomic Weights of Sodium and Chlorine.

The work of Stas upon the atomic weights of a number of the elements has been considered one of the classics of chemistry and, in some cases, a variation from the results obtained by him have been, probably without a satisfactory examination, ascribed to errors in the new determinations. In an article under the above title, by Theodore W. Richards and Roger C. Wells,[1] it is pointed out, regretfully, that this reputation is not entirely deserved, as a careful review of several of the determinations made by Stas show sources of serious error.

This revision was undertaken to throw some light upon the unaccountable discrepancy which appeared in the composition of a sample of very pure sodium bromide, as compared with the results obtained by Stas. While, in some cases, the methods of purification used by Stas are open to criticism and there is a strong probability of the presence of slight impurities in the salts used by him, these are not sufficient to explain the discrepancies in the results, they appear to be due to the method of analysis, rather than to the impurity of the material.

Every preparation of sodium chloride made by Stas was fused in contact with platinum and, in a number of cases, also in the presence of ammonium chloride. The authors show that, under such conditions, a noticeable quantity of platinum is always dissolved. Another source of error, for which the proper correction was not made by Stas, was due to the occlusion of gases by the silver and to impurities probably introduced during the process of removing the mother-liquor from the silver buttons. In the present investigation it is, perhaps, unnecessary to say that the weighing and preparation of material was carried out with all possible precaution. The water was most carefully purified, in some instances being condensed and collected entirely in platinum. Special precautions were taken in the preparation of sodium chloride and silver and, in each case, a number of specimens were made from different sources and by different methods. In the majority of instances a pure salt cannot be obtained by precipitating the impurities, as many assume, but must itself be precipitated or crystallized from the less pure solution. One of the simplest and most satisfactory methods of preparing pure sodium chloride consists in passing hydrochloric acid gas into a strong solution of the salt. A comparison of the material made by this method, with that made by other processes, showed that sodium chloride could be obtained very easily in a pure condition, that water could be expelled from it, by fusion, without loss of halogen and that the salt occludes neither oxygen nor nitrogen.

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[1] Publication 28, of the Carnegie Institution Reports.

The silver used in the experiments was obtained from a number of sources, in some cases being first precipitated as the chloride, which was reduced by invert sugar ; in others being separated by electrolytic methods and, in still others, by the reduction of the nitrate with ammonium formate. All the specimens of silver were, finally, fused in pure hydrogen and then in a vacuum, to remove occluded matter. Dumas pointed out the necessity of fusing silver in a vacuum to remove occluded oxygen and Stas investigated this source of error and introduced a correction for it ; but, in the opinion of the present authors, the correction was not enough, as the silver probably contained as much oxygen as Dumas claimed.

A careful examination of the different methods showed pure lime to be the best support, the amount taken up by the silver being insufficient to affect the results. In testing the solubility of silver chloride and determining its rate of precipitation, the authors selected the method depending upon the intensity of the cloudiness of the opalescent solution, as determined with the nephelometer, an instrument which makes it possible to estimate 1 part of silver chloride in 30,000,000 of water. The solubility was found to vary according to conditions, the presence of sodium nitrate and hydrochloric acid affecting, to a marked extent, the rate at which the intensity of the opalescence increases. The correction for the solubility of silver chloride was applied to the results, although the value was so small as not to affect the third decimal place of the atomic weight of sodium. It is pointed out that Stas' method of dropping solid sodium chloride into a solution of the silver salt is likely to lead to considerable error, because the silver chloride, under these conditions, can occlude large amounts of the salt. They found that, if a moderately concentrated solution of a silver salt is used, or if the precipitate is not washed quickly, the excess of silver salt is enclosed in the silver chloride precipitate, which, upon standing, contracts and envelops the occluded material more securely than at first. Quantitative tests made upon this action of the precipitate showed that, when solutions not stronger than 0.2 N were used and the precipitates were speedily and thoroughly washed, all the silver nitrate, sodium chloride and sodium nitrate could be removed.

Two methods were used to determine the combining weights of sodium chloride, one depending upon the ratio of the sodium chloride to silver chloride, the other upon the ratio of sodium chloride to silver. Every point was carefully tested and all possible precautions taken to avoid error. By the first method the value found for the atomic weight of sodium was 23.017, as compared with 23.048 obtained by Stas.

The authors point out that, in most of the determinations of the ratios between silver and soluble halogen salts, the method of titration has been used. This method, owing to the fact that it involves no collection and weighing of a precipitate, would be capable of great accuracy if the end point were definite.

Stas attempted to attain an intermediate point, between the limits reached, by titrating to the extreme end with sodium chloride and then running back to the opposite limit with silver nitrate. The results obtained in this way varied considerably, however, owing, as the present investigators show, to the fact that sufficient time was not allowed for the opalescent precipitate to reach a point of equality with the standard. Ten determinations are given, with an extreme variation of 0.004 in the values found. These were selected from a large number as the ones in which every known source of error was avoided and where sufficient time had been allowed for the full development of the opalescence. As 7 different specimens of salt and 3 different preparations of silver were used in the determinations, the limit of purity seems to have been reached. Upon the basis of these results, assuming the atomic weight of silver to be 107.93 and that of chlorine 35.455, the atomic weight of sodium is 23.027.

As the two methods gave values which varied by 0.010, a difference far greater than the sum of the probable experimental errors and which also differed by 0.1 per cent from the value obtained by Stas, a further search for the possible source of error was undertaken.

As Stas' determination of the atomic weight of iodine has been shown to be 0.1 per cent too low, the authors thought it advisable to test the accuracy of his determination of the atomic weight of chlorine, by a series of experiments upon the synthesis of silver chloride. In order to avoid any constant error two methods were used, one consisted in the precipitation, filtration and weighing of the silver chloride formed by dissolving pure silver in pure nitric acid and precipitating with hydrochloric acid ; the other depended on the conversion of silver to silver chloride by the same method, but in a quartz vessel in which the silver chloride could be dried and weighed, without any transfer of material during the entire process. Seven determinations by the former method gave 132.8666, while three by the latter gave 132.8673, the mean value, taking into account the "probable errors," being 132.8668.

As a result of these experiments it could be fairly assumed that 100.000 parts of pure silver yield 132.867 parts of silver chloride. Upon this basis, if the atomic weight of silver is taken as 107.92, the atomic weight of chlorine becomes 35.470, a value 0.095 per cent higher than that obtained by Stas.

Since the atomic weight of chlorine has been the standard to which many others have been referred, a difference in its atomic weight would necessitate a change in many others, in fact all weights depending upon the value of silver, chlorine or sodium would be greatly affected in the second decimal place. In the determination of the ratio of silver chloride to sodium chloride, 100.000 grams of silver chloride were obtained from 40.780 grams of sodium chloride. Using the new value for chlorine, the value for sodium becomes 23.004.

By the other method, where the ratio of silver to silver chloride was determined, the value obtained was 23.007. The authors consider the latter more accurate, because no error is introduced, as in the other method, by the occlusion of sodium nitrate.

The new values, as determined by this investigation, are as follows :

	(Ag = 107.92).	(Ag = 107.930.)
Atomic weight of sodium	23.006	23.008
" " " chlorine	35.470	35.473

It is impossible, in a review, to give more than a general idea of the precautions observed in this research. A large part of the pamphlet is taken up with the minute details which are of fundamental importance in such a revision. After reading the paper, one can hardly avoid feeling that, with our present facilities, the limit of experimental accuracy has been reached and an upward step taken toward the exact atomic weights of sodium and chlorine. J. E. G.

REVIEWS.

Einleitung in die Chemische Krystallographie. Von P. Groth. Mit textfiguren. Leipzig : Engelmann. 1904. pp. 80. Price, M4.

The appearance of this little book by Professor Groth, of Munich, is especially timely because of the amount of work which has been done on the subject during the last decades, since the publication of Fock's work of the same title, in 1888, and Arzruni's more exhaustive work, which appeared as part of Graham-Otto's "Lehrbuch der Chemie," in 1893. The present volume possesses an additional value from the clear style and high standing of the author who, as editor of the *Zeitschrift für Krystallographie und Mineralogie*, has kept closely in touch with the recent publications on the problems of chemical crystallography and has himself practically completed an extensive critical and systematic review of all the investigations which have been made on the relations between crystal forms, the properties of crystalline bodies and their chemical constitution. In the present "Introduction" Professor Groth has brought forward the principal "laws" which these investigations have established or suggested, treating them in five chapters dealing, successively, with the general features of Crystal Structure, Polymorphism, Morphotropism, Isomorphism and Molecular Compounds.

The first chapter, on Crystal Structure, discusses the arrangement of molecules in crystalline bodies, the author favoring Sohncke's theory of interwoven latticeworks of similar form, which unite to form lattices of a common type, in which the individual points are themselves complex. In this chapter well-known facts are reviewed to show that many substances, such as sulphur, may crystallize in different forms and these different modifications are divided into two phases, the polysymmetric and the polymorphic, and tests are given for their distinction. The crystals of those *polysymmetrical* forms, in which the twinning intergrowths are no more observable, are only apparently homogeneous bodies and are distinguished from simple or twinned forms of a lower symmetry solely by those properties which are postulated from the latter by the type of structure. Between the two forms may exist transitions with continuously changing properties and it is not necessary that, for every case, there should be a change from one form to the other at a definite temperature.

The polymorphic modifications represent, on the other hand, practically different states (phases). In the change from one to the other one usually finds a discontinuous change of all the properties, both scalar and vectorial and the alteration occurs at a definite temperature, the alteration-point.

The chapter on Polymorphism limits the concept of polymorphism to such homogeneous, physically different states of a body in which the differences rest in differences of their crystal structure. The polymorphous modifications are assigned, primarily, to the temperature conditions, but the influence of the presence of crystallizing points of metastable forms is considered and, following both Ostwald and Scham, Groth explains the formations of metastable modifications, such as monoclinic sulphur, instead of the more stable orthorhombic form, as determined by the positions of the alteration-points on the fusion curves. This explanation is also invoked in the discussion of monotropic and enantiotropic forms. In conclusion, it is recognized that the facts at hand do not warrant the statement of any general law for the relations between the crystal structure and the polymorphic modifications, although the isolated cases carefully studied hold out much hope for fruitful investigations in the future.

The chapter on Morphotropism deals with the dependence of the crystal structure on the chemical constitution of the body. The author here, after describing the changes produced by substitutions as in the nature of homogeneous deformations of the crystal structure, explains the manner of measuring these modifications and gives the morphotropic influence of elements and radicals. The influence on the crystal structure of substituting CH_3, Cl, Br, I, NO_2 or OH for H, is summarized in the following law :

" The alteration, in many cases, occurs appreciably in definite directions, so that one may infer from them something regarding the arrangement of the atoms in the regular structure.

" The type and amount of the deformation depends upon the nature of the entering parts (atoms or atomic groups) and upon the crystal structure of the bodies in which the substitution takes place.

" 1. On the position of the substituted hydrogen atoms in the chemical molecule—thence isomeric bodies possess different crystal structures.

" 2. On the size of the chemical molecule, since the alteration of the crystal structure, in general, is less, the more complicated the compound is, in which the occurring chemical change takes place."

The chapter on Isomorphism includes discussion of (A) the harmony of crystal structure in chemical compounds of analogous constitution ; (B) the relations between crystals and solutions of isomorphous bodies ; (C) Isomorphous Mixtures.

Under this head a few leading investigations, notably the well-known studies of Tutton on the sulphates and selenates of potassium, rubidium and caesium, are reviewed and isomorphic bodies are practically defined as those which show very close agreement in crystal structure because of the similarity of morphotropic effects of related elements. As thus defined there is, manifestly, no sharp limit between isomorphous and morphotropic bodies, but such a definition unites the two types of structural change together and is in harmony with the looser and more general use of the term isomorphism.

Under the second head is briefly discussed the well-known ability of isomorphous substances to grow in solutions of their isomorphs, or to serve as centers of crystallization. These instances are regarded, not as isomorphous growths, as they are often loosely described, but rather as cases of episomorphism and an evidence of the probable isomorphic relations of the substances involved. Isomorphism is really based upon the close similarity of crystal structures and the ability to form homogeneous mixed crystals, in all proportions of the end members.

Under the third head, Isomorphous Mixtures, the author considers the relations between isomorphism and mixed crystals. The discussion seems to involve differences in conception and definition as to what is isomorphism. Van 't Hoff assumes that the mixed crystals are solid solutions in which the laws for gases apply, others hold that the end members are present as individual molecules. Retgers emphasized the complete continuity of the series of mixed crystals, from end member to end member, in which the constituents crystallized in all proportions, the properties of the mixed crystals forming continuous functions of the composition ; Roozeboom and Brune lay stress on the fusion curves, which might apply equally well to certain mixed crystals of non-isomorphous end members. Groth, on the other hand, would include among the "true isomorphous mixtures all those cases in which two substances, which possess no completely analogous chemical composition but a very close affinity of crystal structure, form continuous series of homogeneous mixed crystals, as for example, the triclinic feldspars." This last view would involve an analogy to the polysymmetrical bodies in which we have stable crystals composed of regularly alternating lamellae of sub-microscopic size, which possess the same type of crystal structure.

The discussion of isomorphous mixtures leads, naturally, to that of molecular compounds, but here the treatment seems less satisfactory, chiefly because the relations of the crystal structures of so-called molecular compounds with those of their components have been little investigated. Among the molecular compounds are the racemic salts, consisting of varying amounts of antipodal components leading to active and inactive crystals. The author, following Pasteur, holds that both optical antipodes of an optically active compound possess enantiomorphic crystal structures and, further, that this is a direct consequence of the enantiomorphism of their chemical molecules. Pseudoracemic bodies, with crystal properties, specific gravity and fusion-point similar to those of their component antipodes, are regarded as sub-microscopic intergrowths of the active components. These may be distinguished from true racemates by a comparative study of their solubility and fusion values with those of the active components. E. B. M.

ROCKS, ROCK-WEATHERING AND SOILS. By GEORGE P. MERRILL. New York: Macmillan Company. 1904. pp. 411, illustrated. Price, $4.00.

The appearance of the second edition of this rather unique volume by Professor Merrill is, in itself, an evidence of the value of the work. The book, which has for its theme the changes and processes by which the solid rocks of the earth's crust pass to the more or less incoherent covering of soils, is, at once, a compilation of many scattered data and an original contribution to the subject of rock-weathering. The somewhat unusual scope and the original methods of attack place the book in a field by itself. Other works dealing with rocks or soils as central themes give many facts regarding the passages from the former to the latter, but the author makes the transitions the central point.

The book is divided into five parts dealing, successively, with the constituents and properties of rocks, their kinds, the weathering which they undergo, the methods of removal and redistribution of rock débris and the resulting vegetable or mantle of unconsolidated materials.

In the first two parts the discussion is clear and conservative, well illustrated and well arranged. There is, however, some question as to the propriety of devoting nearly half the entire work to this more distinctly petrographical part, since the matter is available in other works and many of the minerals and rocks described are scarcely, if at all, mentioned in the later portions of the volume.

The third part of the book, dealing with the weathering of the rocks, containing as it does a discussion of the principles, manifestations and conditions of weathering, is the best of the whole. Most of the material is new and much of it is the result of the author's own investigations. In this portion of the book are many new analyses of rocks and especially analyses of the same rock in different stages of degeneration. The manner of computing the relative loss of constituents, during rock-weathering, is of especial interest. It is assumed, with reason, that alumina and ferric iron are the most stable and that relatively little of these constituents has been removed. On this basis the relative removal of the remaining constituents has been computed. The most important changes indicated are hydration, a loss in silica, a relatively greater loss in lime, magnesia and the alkalies and an apparent gain in alumina and, occasionally, iron. The cumulative effect is a decided loss of materials, which may amount to 50 per cent of siliceous rocks and even 99 per cent, in extreme cases, of calcareous rocks.

The discussion of transportation and redistribution occupies but a few pages, although containing many facts regarding the different agents at work.

The treatment of the Regiolith, including the discussion of soils is good, though, possibly, somewhat disappointing to certain soil investigators.

The book, as a whole, is an excellent piece of work, well thought out, clearly expressed, admirably illustrated and well published. It is, however, to be regretted that the press of other duties did not permit the author to bring the subject up to date in this later edition.

E. B. M.

see errata p. 625

THE CHEMICAL SYNTHESIS OF VITAL PRODUCTS AND THE INTER-RELATIONS BETWEEN ORGANIC COMPOUNDS. By RAPHAEL MELDOLA- F.R.S., V.P.C.S., F.I.C., Professor of Chemistry in the City and Guild, of London Technical College, Finsbury; Member of the Faculty of Science, University of London, etc. Vol. I.: Hydrocarbons, Alcohols and Phenols, Aldehydes, Ketones, Carbohydrates and Glucosides, Sulphur and Cyanogen Compounds, Camphor and Terpenes, Coloring Matters of the Flavone Group. London: Edward Arnold. 1904. pp. 338. Price, 21 shillings, net.

The author has imposed upon himself a most laborious task in the preparation of this work. It is a reference book in which are catalogued only those organic substances that have been produced synthetically and which occur in living things, whether animal or vegetable, or are produced by the growth of microörganisms. No theories are considered and the author limits himself to the statement of facts. The occurrence and methods of synthesis are tabulated under each compound, together with copious references to the very scattered literature on this subject.

A few quotations from the introduction will make clear the scope and aim of the work. "It is in no sense to be regarded as a critical work and my whole object has been to bring practical workers, whether chemists, physiologists or technologists into communication with the authorities quoted." The term "vital product" is used by the author in a broad sense and "has been enlarged so as to include every atomic complex which, without unduly straining the facts, there is reason for believing to be present in the products resulting from vital synthesis, the other condition for insuring inclusion in this work being, of course, that the complex has been synthesized in the laboratory." Thus salicylic acid and methyl alcohol are included in this work, on account of the occurrence of methyl salicylate, although neither have been found to occur in the free state.

The author points out that pyrogenic syntheses and those accomplished by the use of violent reagents do not resemble, in any way, the vital syntheses and are, therefore, from a biochemical point of view, of little interest. Hence, the ordinary chemical classification and arrangement are laid aside and the substances which are genetically related are brought together, regardless of the type of the compounds. "The treatment of organic chemistry in this work has accordingly been entirely subordinated to the biochemical view of the subject." The author states that he is "not without hope that this work may be found of service as a step towards the foundation of a more exact science of biochemistry" and "that the present résumé will materially assist any future discussion of the problems of biochemistry." These are very high hopes for a work of this character. It will, undoubtedly, prove of much value as a book of reference and should be within reach of all who are working in this field. Only a more extended usage can determine how thoroughly and carefully the work of compilation has been done. The second volume, which will complete the work, is now in preparation. A. S. L.

THE FOLLIES OF SCIENCE AT THE COURT OF RUDOLPH II. By HENRY CARRINGTON BOLTON. Milwaukee: Pharmaceutical Review Publishing Company. 1904. pp. 217.

In this book an attempt has been made to give some account of the character of the scientific atmosphere pervading the Court of Rudolph II, Emperor of Germany. To the chemist it will be of special interest for the reason that it deals, to a considerable extent, with alchemy. Alchemy has been called one of the six follies of science, the others being the quadrature of the circle, the multiplication of the cube, perpetual motion, judicial astrology and magic. The author says: "Alchemy, after astrology, probably contributed more directly than any other of the six follies of science towards the advancement of the genuine science associated with it."

The book will be found interesting not only by the chemist but by the general reader, as it is not rendered incomprehensible by the use of technical language. I. R.

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AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

THE TITRATION OF FERROUS IRON WITH PERMANGANATE IN THE PRESENCE OF HYDROCHLORIC ACID.

BY GREGORY PAUL BAXTER AND HARRY LOUIS FREVERT.

Recent investigation in this laboratory upon the titration of oxalic acid with potassium permanganate, in the presence of hydrochloric acid, has shown that this operation may be accurately performed without the addition of manganous salts, provided the temperature of the solution of oxalic acid, at the beginning of the titration, is above 70°.[1] With the idea that a similar procedure might be successfully applied to the titration of ferrous iron, under the same conditions, the following experiments were carried out :

A solution of ferrous chloride, containing approximately 0.01 gram in 1 cc., was prepared by reducing ferric chloride with iron, wire, in the presence of hydrochloric acid. The solution contained sufficient hydrochloric acid for the subsequent oxidation of the iron. Potassium permanganate solutions used in the oxidation contained, approximately, 4 grams of salt per liter.

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[1] Baxter and Zanetti : THIS JOURNAL, 33, 500 (1905).

The relative strengths of the ferrous chloride and permanganate solutions were determined by slowly adding permanganate, from a burette, to 25 cc. portions of the ferrous solution, which had been diluted to 150 cc. by introducing the ferrous chloride, from a pipette, into the requisite amount of a boiling solution of 1 gram of manganous chloride crystals. It has already been shown, by various experimenters, that potassium permanganate may be used for the accurate estimation of iron, in the presence of hydrochloric acid, provided the solution contains sufficient manganous salt.[1]

In order, as far as possible, to avoid oxidation of the ferrous solution by the air, the titrations were performed in Erlenmeyer flasks. Since, even in the cold, the ferrous solution slowly changed in strength, comparisons of the permanganate and ferrous chloride were always made immediately before the use of the solutions. The change of color from the yellow of the ferric solution to the purplish-yellow, due to the presence of an excess of permanganate, is sharp and affords a very satisfactory end-point; but, even for a practised eye, a "standard end-point" makes the change more easily detected.

Titrations were first made to determine whether, in the case of iron as in the case of oxalic acid, the amount of permanganate required was dependent upon the temperature. In each experiment the ferrous solution was diluted by addition to warm or hot freshly boiled, distilled water. In analyses 10 and 11 the solution was heated to boiling subsequently to dilution with boiling water. No manganous salt was added in any case. The recorded temperature is that at the beginning of the titration. In all the experiments below 70° a distinct odor of hypochlorous acid was perceptible.

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[1] Kessler: Ann. Phys., **194**, 48 (1863); **195**, 225 (1863); Zimmermann: Ann. Chem. (Liebig), **213**, 305 (1882); Wagner: Z. physik. Chem., **28**, 60 (1899); Gooch and Peters: Am. J. Sci., **7**, 461 (1899).

Table I.

Number of analysis.	Volume of solution. cc.	Temperature. Degrees.	$KMnO_4$ used. cc.	$KMnO_4$ theory. cc.	Error. Per cent.
1	150	30	37·52	37.16	1.0
2	"	30	37·58	"	1.1
3	"	29	37·48	"	0.9
4	"	58	37·41	"	0·7
5	"	69	37·35	"	0·5
6	"	78	37·30	"	9·4
7	"	85	37·26	"	0·3
8	"	85	37·25	"	0.2
9	"	88	37·24	"	0.2
10	"	97	37·29	"	0·3
11	"	100	37·28	"	0·3
12	"	85	39·59	39·51	0.2
13	"	84	39·60	"	0.2
14	"	81	39·94	39·85	0.2
15	"	85	39·97	"	0·3
16	"	83	39·96	39·76	0·5

It is evident, from the above results, that the error increases with diminishing temperature, as in the case of oxalic acid,[1] but that, even at the highest possible temperatures, the excess of permanganate required amounts to between 0.2 and 0.3 per cent.

With the hope that increasing the volume of the ferrous solution might have a beneficial effect, several titrations were performed where the volume of the ferrous solution was both greater and less than 150 cc. In analyses 17, 18 and 19 the solution was heated to the recorded temperature, after dilution.

Table II.

Number of analysis.	Volume of solution. cc.	Temperature. Degrees.	$KMnO_4$ used. cc.	$KMnO_4$ theory. cc.	Error. Per cent.
17	50	87	36.86	36.77	0.2
18	50	95	36.89	"	0.3
19	100	97	36.87	"	0.3
20	300	87	36.85	"	0.2

These experiments show that the dilution is without effect upon the magnitude of the error.

It was to be expected that the error would increase with increasing hydrochloric acid concentration. Contrary to expectation the quantities of permanganate used were slightly smaller when a considerable excess of hydrochloric acid (sp. gr. 1.04–5) was added before titration. When more than 40 cc. were employed the end-point became uncertain.

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[1] *Loc. cit.*

Table III.

Number of analysis.	Volume of solution. cc.	Temperature. Degrees.	HCl added. cc.	$KMnO_4$ used. cc.	$KMnO_4$ theory. cc.	Error. Per cent.
21	150	83	. .	36.02	35.86	0.4
22	"	85	. .	36.00	"	0.4
23	"	"	. .	36.02	"	0.4
24	"	"	10	36.00	"	0.4
25	"	"	20	36.02	"	0.4
26	"	"	20	36.02	"	0.4
27	"	"	30	36.03	"	0.5
28	"	"	30	36.02	"	0.4
29	"	"	40	35.93	"	0.2
30	"	"	40	35.95	"	0.3
31	"	"	30	39.11	39.02	0.2
32	"	"	30	39.10	"	0.2
33	"	"	40	39.10	"	0.2
34	"	"	40	39.10	"	0.2
35	"	"	. .	39.20	"	0.5
36	"	"	. .	39.18	"	0.4

Finally, the effect of varying temperature and dilution, in the presence of varying amounts of both manganous sulphate and chloride, was determined (see Table IV., on opposite page).

From the results of the above experiments it can be seen, first, that neither the temperature of the solution nor the dilution is important if sufficient manganous salt is present; secondly, that although, at 97°, 0.5 gram of crystallized manganous chloride is sufficient to prevent loss of chlorine, at lower temperatures accurate results can be obtained only in the presence of at least 1 gram of this salt; and, finally, that manganous sulphate is more effective than manganous chloride in preventing the error, 0.5 gram of the former being sufficient at a dilution of 150 cc., at 85°.

In the previous paper upon the titration of oxalic acid in the presence of hydrochloric acid, the hypothesis was advanced

Table IV.

Number of analysis.	Volume of solution. cc.	Temperature. Degrees.	$MnCl_2.4H_2O$ added. Grams.	$MnSO_4.5H_2O$ added. Gram.	$KMnO_4$ used. cc.	$KMnO_4$ theory. cc.	Error. Per cent.
37	150	30	1.0		37.17	37.16	0.0
38	“	29	“		37.16	“	0.0
39	“	84	“		37.17	“	0.0
40	“	83	“		37.15	“	0.0
41	“	85	“		37.15	“	0 0
42	300	88	“		36.78	36.77	0.0
43	50	93	“		36.76	“	0.0
44	“	92	“		36.77	“	0.0
45	100	94	“		36.77	“	0.0
46	150	80	0.5		39.48	39.51	—0.1
47	“	83	“		39.51	“	0.0
48	“	84	“		39.51	“	0.0
49	“	83	“		39.92	39.76	0.4
50	“	85	“		39.91	“	0.4
51	“	85	“		39.10	39.02	0.2
52	“	85	“		39.10	“	0.2
53	“	85	“		39.10	“	0.2
54	“	97	“		37.17	37.16	0.0
55	“	97	“		37.16	“	0.0
56	“	85	1.0		39.73	39.76	—0.1
57	“	80	2.0		39.75	“	0.0
58	“	85	3.0		39.79	“	0.1
59	“	85	4.0		39.76	“	0.0
60	“	80	1.0		39.82	39.84	—0.1
61	“	82	2.0		39.83	“	0.0
62	“	81	3.0		39.86	“	+0.1
63	“	85	1.0		36.88	36.77	0.3
64	“	87	1.0		36.93	“	0.4
65	“	85	1.0		36.68	“	—0.2
66	“	85	2.0		36.80	“	0.1
67	“	85	2.0		36.75	“	—0.1
68	“	82	2.0		36.77	“	0.0
69	“	86	3.0		36.75	“	—0.1
70	“	86		0.5	36.74	36.73	0.0
71	“	85		0.5	36.73	“	0.0
72	“	86		1.0	36.73	“	0.0
73	“	87		0.5	34.73	34.70	0.1
74	“	86		0.5	34.70	“	0.0
75	“	87		0.5	34.70	“	0.0
76	“	87		0.5	34.71	“	0.0
77	“	86		1.0	34.71	“	0.0
78	“	87		1.0	34.70	“	0.0

that, at low temperatures, the use of an excess of permanganate over that theoretically necessary is due to the volatilization of hypochlorous acid, produced by the action of the permanganate upon the hydrochloric acid ; and that, at high temperatures, this loss is prevented by the more rapid action of the permanganate upon the manganous salts, produced by the reduction of the permanganate, to form compounds of trivalent or quadrivalent manganese which, in turn, are capable of rapidly oxidizing the oxalic acid. In the course of the present investigation additional evidence was obtained which supports this hypothesis.

In the first place it was shown that permanganates may be formed by the interaction of hypochlorites and manganous salts, by bringing together calcium hypochlorite and manganous chloride, in the presence of much alkali. Since acids accelerate the reduction of potassium permanganate by chlorides, alkalies should hasten the reverse process. To a concentrated solution of manganous chloride much sodium hydroxide and calcium hypochlorite were added. The pasty mass was then heated upon the steam-bath for some time. When the product was diluted a solution of sodium permanganate, of considerable concentration, was obtained. That this permanganate was not due to possible chlorates from the transformation of the hypochlorites was certain, since a repetition of the experiment, with potassium chlorate in place of the calcium hypochlorite, gave no trace of permanganate.

Although this proof that the possible reaction of permanganate upon hydrochloric acid, to produce hypochlorous acid, is reversible, does not make it absolutely certain that the reduction of the permanganate actually takes place in this way, a few simple experiments gave positive evidence that this is the case. To separate solutions of oxalic acid and ferrous sulphate, at room temperature, strong, concentrated chlorine water was added. When tested with starch iodide paper, after a few seconds, not even a trace of chlorine could be detected. On the other hand, when a solution of calcium hypochlorite was added to similar solutions of oxalic acid and ferrous sulphate, both of which had been made acid with hydrochloric acid, the odor of hypochlorous acid was marked and persistent for some time, although, eventually, the hypochlorous acid was reduced in both cases. Obviously, since chlorine is taken up almost instantly by both oxalic acid and ferrous sulphate, in the latter experiment the solutions could not have contained free chlorine. The odor which is plainly perceptible at the beginning of titrations, at low temperatures, with permanganate in the presence of hydrochloric acid must, therefore, be due to hypochlorous acid and not to chlorine, as is commonly assumed.

On the other hand, manganous salts were found to have no appreciable effect. For, when acid solutions of oxalic acid and ferrous sulphate, to both of which manganous sulphate had been added, were treated with calcium hypochlorite, hypochlorous acid could be detected for the same length of time as with solutions, otherwise exactly similar, but containing no manganous sulphate. Since the oxidation by hypochlorous acid takes place at the same rate whether manganous salts are present or not, it is evident that the beneficial effect of manganous salts, in titrations with permanganate, is due to acceleration of the reaction of the *permanganate* upon the manganous salts, as proposed originally by Zimmermann,[1] and subsequently maintained by other investigators,[2] as well as in this paper.

Upon heating the solutions of oxalic acid and ferrous sulphate, containing hypochlorous acid, the hypochlorous acid disappeared by reduction and, when calcium hypochlorite was added to hot acid solutions of the reducing agents, the reaction was practically instantaneous.

Experiments 21 to 36, in which it was found that, up to a certain point, increasing the concentration of the hydrochloric acid diminishes the error, indicate that, under these conditions, the reaction between hypochlorous and hydrochloric acids to produce chlorine is considerably accelerated.

The above experiments show, conclusively, that the loss of chlorine, during titrations with permanganate in the presence of hydrochloric acid, together with the consequent positive error in the quantity of permanganate employed, is not due to volatilization of free chlorine from the solution, but to the formation and volatilization of hypochlorous acid. The catalytic effect of manganous salts is the result of the production of some intermediate manganic compound, through the action of the permanganate. Finally, the oxidation of oxalic acid and ferrous iron, under the conditions which have been described, takes place chiefly through the agency of the above-mentioned manganic compound, although, undoubtedly, both permanganate and hypochlorous acid are capable of acting directly upon either oxalic acid or ferrous salts. Obviously the rate of oxidation is dependent upon the velocities of all the reactions involved. In the case of oxalic acid, even without the addition of manganous salts, it has been found possible, by the use of high temperatures, to accelerate the Guyard reaction of permanganate upon manganous salts to such an extent as to avoid appreciable formation and loss of hypochlorous acid by volatilization. Unfortunately, in the case of ferrous salts, a similar remedy was found to give less satisfactory results.

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[1] Ann. Chem. (Liebig), **213**, 305 (1882).

[2] Wagner: Z. physik. Chem., **28**, 1 (1899); Gooch and Peters: Am. J. Sci., **7**, 461 (1899).

Summary.

The results of the foregoing research are, then, as follows:

1. It is found that, even at the highest possible temperatures, the accurate estimation of ferrous iron, by titration with permanganate, in the presence of hydrochloric acid, is impossible without the introduction of manganous salts.

2. The results obtained at 80°–90° are however, about 0.3 per cent. too high, so that titrations carried out in this fashion may be corrected, with considerable exactness, by applying a negative correction of 0.3 per cent., if the concentration of the hydrochloric acid is not too great.

3. It is found that, except at temperatures in the neighborhood of 95°, 0.5 gram of manganous chloride is insufficient completely to eliminate the error, but that 1 gram of this salt

yields accurate results at all temperatures. On the other hand, 0.5 gram of manganous sulphate is a sufficient quantity.

4. The hypothesis previously proposed that, in the titration of oxalic acid and ferrous iron, in hydrochloric acid solution, by permanganate, the error, in the absence of manganous salts, is due to the production of hypochlorous acid and volatilization of this substance from the solution, receives further support.

CAMBRIDGE, MASS.,
April, 26, 1905.

Contributions from the Sheffield Laboratory of Yale University.

CXXIV.—ON SOME URAZOLE AND IMIDOTHIOBIAZOLINE DERIVATIVES.

BY HENRY L. WHEELER AND JOANNES G. STATIROPOULOS.

In a paper on phenylthiosemicarbazidic esters, which was published five years ago, Wheeler and Dustin described the preparation of three compounds of unknown constitution. Two of them were provisionally represented as imidothiobiazolines, the other as a urazole derivative.[1] Further work on the structure of these compounds has now established the fact that the so-called biazoline derivatives are really urazoles, while the compound described as a urazole in all probability is an imidothiobiazoline. In the study of the somewhat confusing reactions which lead either to an imidobiazoline or a triazole condensation we have also been impressed with the fact that little can be expected from analogy.

The first compound to be considered was originally obtained by combining phenyl isocyanate with ethyl phenylthioncarbazinate $C_6H_5NH.NHCS.OC_2H_5$, this gave ethyl *c,b*-diphenyl-α-thionsemicarbazidate, $C_6H_5NHCO(C_6H_5)N.NHCS.OC_2H_5$. When this substance was treated with sodium ethylate, with or without ethyl bromide, a compound melting at 86° resulted, which was free from sulphur. This, on analysis, gave results agreeing with the calculated for 1,4-diphenyl-3-ethoxyurazole, I, or α-ethoxy-α'-phenylimido-β'-phenyloxybiazoline II.

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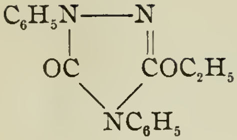
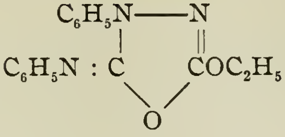
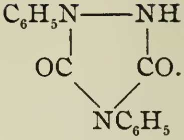
[1] THIS JOURNAL, **24**, 430 (1900).



I.



II.



III.

We have now found that the substance gives 1,4-diphenylurazole, III, melting at 163°, when boiled with hydrobromic acid, the product being identical with the compound described by Busch and Holzmann[1] and later obtained by other methods,[2] notably by desulphurizing 1,4-diphenyl-5-thiourazole[3] with potassium permanganate.

We have prepared the substance represented by Formula I by treating the silver salt of 1,4-diphenylurazole with ethyl bromide and we find that it is identical with the material melting at 86°, described in our previous paper.

This shows that the substance is a triazole, or rather a urazole, because it excludes the possibility that the material is a biazoline which, on hydrolysis, rearranges to the diphenylurazole.

We did not obtain this 1,4-diphenyl-3-ethoxyurazole on treating the sodium salt of the urazole with ethyl bromide, at 100°, but found instead that an isomeric nitrogen derivative resulted. It is, therefore, probable that Busch's corresponding methyl derivative,[4] prepared under similar conditions, has the alkyl group attached to nitrogen and not, as he represents, to oxygen.

The next compound prepared by Wheeler and Dustin to be considered was originally obtained by treating the above mentioned ethyl *c*,*b*-diphenyl-*a*-thionsemicarbazidate with aqueous alkali and benzyl chloride. This operation gave a product melting at 110°–112°, containing sulphur and which agreed in composition with a compound represented by Formula IV or V.

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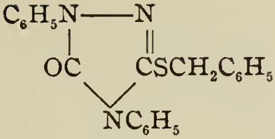
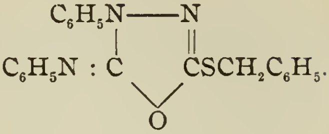
[1] Ber. d. chem. Ges., **34**, 341 (1901).

[2] Busch and Heinrichs: *Ibid.*, **34**, 2336.

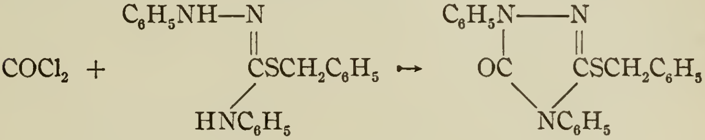
[3] Busch: *Ibid.*, **35**, 973 (1902).

[4] *Ibid.*, **34**, 2337.


IV.

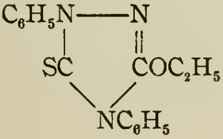

V.

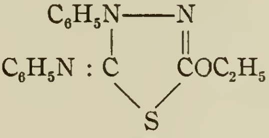
The following synthesis now proves conclusively that this substance is to be represented by Formula IV, in other words, it is 1,4-diphenyl-3-benzylmercaptourazole. Diphenylthiosemicarbazide was combined with benzyl chloride, giving diphenylpseudobenzylthiosemicarbazide hydrochloride, and this substance, with alkali and phosgene, reacted as follows:

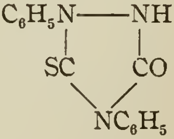

VI.

The compound thus obtained was identical in every respect with the one obtained by Wheeler and Dustin, melting at 110°–112°.

We found when ethylphenylthioncarbazinate, $C_6H_5NH.NH.CS.OC_2H_5$,[1] was treated with phenyl mustard oil that hydrogen sulphide was evolved and a compound, melting at 83°, resulted. Analysis indicated that this was either a urazole, VII., or an imidothiobiazoline, VIII.


VII.


VIII.


IX.

When this substance was boiled with hydrobromic acid 1,4-diphenyl-5-thiourazole, IX, melting at 216°–221°, was obtained.[2]

Marckwald[3] and Busch and Holzmann[3] found that this substance, IX, on methylating, gave a product having the alkyl group attached to sulphur; it readily eliminated mercaptan, yielding 1,4-diphenylurazole, III. This excludes the biazoline formula for these compounds and leads to the conclusion that our compound, melting at 83°, is 1,4-diphenyl-3-ethoxy-5-thiourazole, VII.

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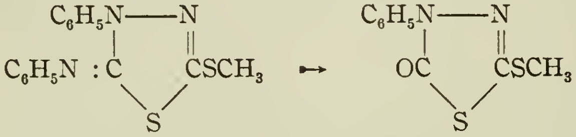
[1] Wheeler and Barnes: This Journal, **24**, 65 (1900).

[2] Marckwald: Ber. d. chem. Ges., **25**, 3109 (1892); Busch, Holzmann: *Ibid.*, **34**, 326; **34**, 2328; **35**, 974 (1902).

[3] *Loc. cit.*

It may be stated, in connection with the hydrolysis of the material melting at 83°, that Busch and Wolpert[1] found their "phenylthiobiazolon-anil-thiomethan" X, which has a structure analogous to VIII, did not give a urazole when boiled with hydrochloric acid. The compound yielded aniline instead, giving a thiobiazoline represented by formula XI, which shows that, in this case, the hydrolysis does not involve a molecular rearrangement.


X. XI.

It is noteworthy that the compound, VII, melting at 83° and also the urazole, IX, melting at 216°–221°, were obtained together when isocyanphenyl chloride, $C_6H_5NCCl_2$ was allowed to act on ethyl phenylthioncarbazinate. According to Freund and König,[2] the action of isocyanphenyl chloride on acyl compounds of phenyl hydrazine yields biazoline derivatives. It may be added, however, that Busch and Wolpert found, according to the choice of certain conditions, either a biazolon, or a urazole could be obtained by the action of mustard oils on dithiocarbazinic acids.

The third substance of unknown constitution, described by Wheeler and Dustin, was obtained by the action of benzoyl isothiocyanate, C_6H_5CONCS, on ethyl thioncarbazinic ester. Hydrogen sulphide was evolved and a compound melting at 138° resulted. This agreed in composition with the urazole, XII, or the imidothiobiazoline, XIII. From analogy to the above, that is the behavior of phenyl isothiocyanate towards ethyl phenylthioncarbazinic ester, this compound should be a urazole, but the properties of the substance which have now been determined are not reconcilable with this view.

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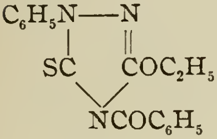
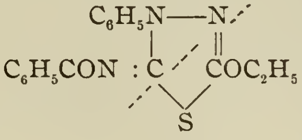
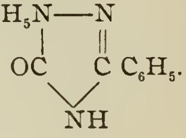
[1] Ber. d. chem. Ges., **34**, 306 (1901).

[2] *Ibid.*, **26**, 2869 (1893).

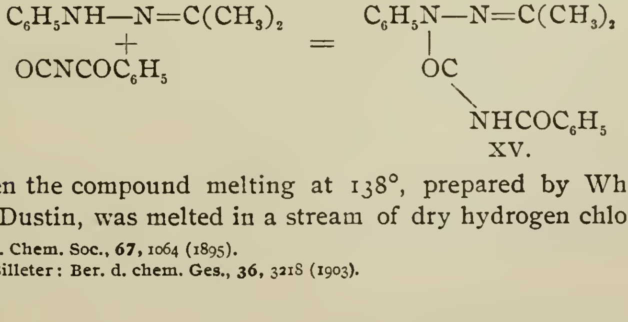

XII.


XIII.


XIV.

With the expectation of obtaining 1-phenyl-5-thiourazole we boiled the substance, melting at 138°, with hydrobromic acid. A product, free from sulphur, was obtained. This agreed in composition with a diphenyloxytriazole. It melted at 229°–230° and, therefore, was not identical with the known 1,5-diphenyl-3-oxytriazole described by Young.[1] The new isomer, or 1,3-diphenyl-5-oxytriazole, XIV, was prepared and it was then found that this was the material which resulted from the hydrolysis with hydrobromic acid. Since the urazole ring is very stable towards acids, this curious behavior, which, in either case, involves a rupture of the ring and a subsequent condensation, is best explained by the biazoline structure, XIII., the cleavage taking place as shown by the dotted line

The new 1,3-diphenyl-5-oxytriazole was prepared by combining benzoyl isocyanate, C_6H_5CONCO[2] with acetone phenylhydrazone. The resulting benzoylphenylsemicarbazone, XV, on warming with a little dilute hydrochloric acid, evolved acetone and condensed, forming the triazole melting at 229°–230°.


XV.

When the compound melting at 138°, prepared by Wheeler and Dustin, was melted in a stream of dry hydrogen chloride, ethyl chloride was given off and a compound agreeing in composition with the imidobiazolon, XVI, or the urazole, XVII, was obtained. This melted at 206°.

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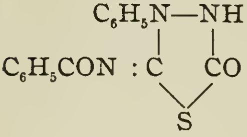
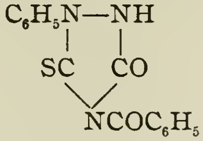
[1] J. Chem. Soc., **67**, 1064 (1895).

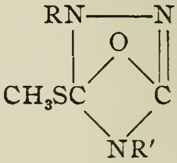
[2] Billeter: Ber. d. chem. Ges., **36**, 3218 (1903).



XVI.



XVII.

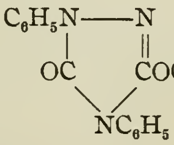


XVIII.

Busch[1] has shown that compounds, such as IX or XVII, that is to say 1,4-disubstituted-5-thiourazoles, on methylation, give thioethers. These are represented by Formula XVIII, in which the alkyl group is attached to sulphur. This is evident from the fact that they readily separate mercaptan. We find that our material, on alkylating with ethyl iodide and alkali, at 100°, does not give a thioether, but regenerates the compound melting at 138°. We conclude, from this result and from the behavior of the material on hydrolysis with hydrobromic acid, that the substance described by Wheeler and Dustin, melting at 138°, is α-ethoxy-α'-benzoylimido-β'-phenylthiobiazoline, XIII, and not a urazole derivative, while the diethylated product obtained from it, melting at 206°, is α'-benzoylimido-β'-phenylthiobiazolon, XVI. The fact that this latter substance is decomposed by boiling alkali and that 1-phenyl-4-thiourazole was not obtained, lends further support to the biazoline structure for these compounds.

The absence of analogy in the behavior of phenyl isothiocyanate and of benzoyl isothiocyanate towards ethyl phenylthioncarbazinate recalls the similar reactions of α-diphenylthiosemicarbazide with phosgene, whereby 1,4-diphenyl-5-thiourazole is formed and, on the other hand, with thiophosgene, which results in the formation of a thiobiazolon.[2]

EXPERIMENTAL.

1,4-Diphenyl-3-ethoxyurazole,  .—1,4-Di-

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[1] Ber. d. chem. Ges., **35**, 975 (1902); Busch and Opfermann: *Ibid.*, **37**, 2333 (1904).

[2] Busch and Holzmann: *Ibid.*, **34**, 326 (1901).

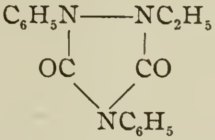
phenylurazole was prepared from phenyl isocyanate and ethyl phenylcarbazinate, as described by Busch and Heinrichs.[1] Six and one-half grams of this substance were suspended in alcohol and an alcoholic solution of 0.6 gram of sodium was added, whereupon a clear solution resulted. This was poured, with vigorous stirring, into a solution of 4.4 grams of silver nitrate, in 250 cc. of water. A fine, brownish-gray precipitate separated which was allowed to settle and was washed by decantation and then on the filter. It was dried over sulphuric acid, suspended in ether and allowed to remain with an excess of ethyl iodide, in the cold, for several days. The ether solution, on evaporation, left an oily residue which solidified. This was washed with alkali and water. On crystallizing from alcohol, long, slender, colorless prisms were obtained, which softened at 83°–85° and melted, to a clear oil, at 85°–86°.

Analysis:

	Calculated for $C_{16}H_{15}O_2N_3$.	Found.
N	14.95	15.36

This compound proved to be identical with the substance described in a previous article as α-ethoxy-α'-phenylimido-β'-phenyloxybiazoline.[2] A small sample of this material, left by Mr. Dustin, was boiled with strong hydrobromic acid for a few minutes. The acid was evaporated and the residue was boiled with petroleum ether and crystallized from alcohol. It then melted at 163° and had all the properties of 1,4-diphenylurazole.

1,4-Diphenyl-2-ethylurazole,



.—Three grams of 1,4-diphenylurazole were dissolved in 1 molecular proportion of alcoholic sodium hydroxide and an excess of ethyl bromide was added. This solution was heated at 100°, for 3 hours, whereupon the contents of the tube gave a neutral reaction. The alcohol was evaporated and the residue was treated with water; this left a reddish-colored oil, which solidified and, on crystallizing from alcohol, colorless glistening prisms were obtained, melting at 125°–126°. Analysis:

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[1] Ber. d. chem. Ges., **34**, 2335 (1901).

[2] This JOURNAL, **24**, 442 (1900).

	Calculated for $C_{16}H_{15}O_2N_3$.	Found.
N	14.95	15.28

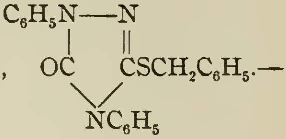
This material is readily soluble in alcohol, ether and benzene. It is moderately soluble in hot water and practically insoluble in cold. It remained unaffected when boiled with hydrobromic acid.

The Benzyl Chloride Addition-product of Diphenylthiosemicarbazide, $C_6H_5NHNHCCl(SCH_2C_6H_5)NHC_6H_5$. — Ten grams of finely-powdered diphenylthiosemicarbazide were moistened with dry benzene and 3.3 grams of benzyl chloride were added. The mixture was digested on the steam-bath and in a few hours all went into solution. At the end of 8–9 hours a finely divided, white powder separated. This was washed with ether, whereupon it melted at 149°–150°. The substance is readily soluble in alcohol. Analysis:

	Calculated for $C_{20}H_{20}N_3SCl$.	Found.
N	11.37	11.69

The free pseudobenzylthiosemicarbazide is very unstable. In the air it rapidly oxidizes, giving deep red solutions. When the above experiment was repeated, using alcohol as a solvent, the addition was complete in an hour. The alcoholic solution was evaporated to dryness and a light yellow, oily residue was obtained which, on cooling, hardened to a resinous mass. This was stirred with sodium hydroxide and ether and the ether was dried over calcium chloride. A portion of this solution was evaporated and a reddish, oily residue was obtained which did not crystallize satisfactorily from any solvent. By dissolving some of the benzyl chloride addition-product in alcohol, cooling in a freezing-mixture and neutralizing with dilute sodium hydroxide, at first a white turbidity resulted, then a yellowish oil, which very soon turned bright red. On remaining exposed in the freezing-mixture for several hours, a few bright red needles were obtained, melting at about 55°. This substance, which was undoubtedly the azo derivative, $C_6H_5N : N.C(SCH_2C_6H_5) : NC_6H_5$, was not further examined.

1,4-Diphenyl-3-benzylmercaptourazole,

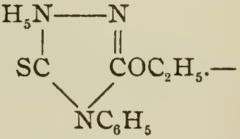


The main portion of the above ether solution of the free pseudothiosemicarbazide was shaken with a solution of phosgene in toluene and an excess of alkali. The phosgene solution being added in small portions, until it gave no precipitate in the ether. The ether and toluene were then evaporated and, on cooling, the oily residue solidified. This was crystallized several times from alcohol, when fine, long, shining needles were obtained, melting at 110°–112°. Analysis:

	Calculated for $C_{21}H_{17}ON_3S$.	Found.
N	11.69	11.55

This proved to be the substance obtained by Wheeler and Dustin, when ethyl *c,b*-diphenyl-α-thionsemicarbazidate was treated with alkali and benzyl chloride.[1]

1,4-Diphenyl-3-ethoxy-5-thiourazole,



Five grams of ethyl phenylthioncarbazinate and 3.5 grams of phenyl mustard oil were heated on the steam-bath, for about 6 hours. Hydrogen sulphide was evolved and an oil resulted. On cooling in a freezing-mixture crystals separated which were washed with ether and found to be diphenylthiourea. The ether left, on evaporation, a thick, yellow oil which was extracted with dilute hydrochloric acid. This extract was neutralized with sodium hydroxide, the oil which separated, on cooling in a freezing-mixture, solidified. It was crystallized once from alcohol, then dissolved in ether and left to crystallize by spontaneous evaporation. In this manner large, well-developed pyramids were obtained, melting at 83°. Dr. W. E. Ford has kindly furnished us with the following crystallographical description:

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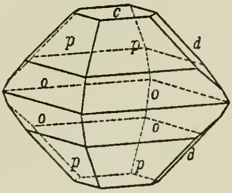
[1] THIS JOURNAL, 24, 442 (1900).

The crystals are orthorhombic in symmetry, showing a simple combination of base, c (001), two pyramids, ρ (111), and o (221), with brachydome d (011). Their habit is illustrated by the accompanying figure. The crystals were well developed, having a diameter of 5 mm. The faces were somewhat etched, but gave fairly distinct signals on the reflection goniometer. The following angles were measured:



Measured.	Calculated.
$c\ (001) \wedge \rho\ (111) = 55°50'$ *	
$c\ (001) \wedge o\ (221) = 71°19'$	$71°34\frac{3}{4}'$
$c\ (001) \wedge d\ (011) = 45°20\frac{1}{2}'$ *	
$d\ (011) \wedge \rho\ (111) = 36°50'$	$36°58'$

Using the measurements marked by an asterisk as fundamental, the axial ratio was calculated as:

$$a : b : c = 0.9528 : 1.00 : 1.012.$$

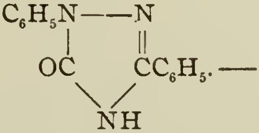
Considering the rather poor quality of the faces the agreement between the calculated and measured angles, as indicated in the above table, is sufficiently close.

This substance was also obtained by Dr. T. B. Johnson, as follows: *Isocyanphenyl chloride* and *ethyl phenylthioncarbazinate*, 3.5 grams of the latter and 3.1 grams of the former, were mixed in dry benzene and allowed to stand at ordinary temperatures. The action took place slowly and hydrogen chloride was evolved, the solution assumed a red color and became turbid. The mixture was warmed on the steam-bath, this caused a violent effervescence, ethyl chloride and hydrogen sulphide were evolved. After the evolution of gas had ceased the product was a thick oil. It was washed with sodium hydroxide, whereupon the oily, insoluble material solidified on standing. It crystallized from alcohol in beautiful prisms and melted at 83°. It had all the properties of the compound above mentioned. Analysis:

	Calculated for $C_{16}H_{15}ON_3S$.	Found.
N	14.14	13.88

The material is readily soluble in alcohol, less readily in ether and insoluble in water; when boiled with hydrobromic acid it gave *1,4-diphenyl-5-thiourazole,* melting at about 215°. The same substance was obtained on treating the fused material, at 85°–95°, with dry hydrogen chloride. It was also obtained as a product of the above reaction, it being removed by the treatment with alkali. Analysis:

	Calculated for $C_{14}H_{11}ON_3S$.	Found.
N	15.6	15.3

1,3-Diphenyl-5-oxytriazole,  —Three grams of the substance described by Wheeler and Dustin, melting at 136°–138°, was boiled, for about 8 minutes, with strong hydrobromic acid, whereupon crystals of benzoic acid condensed at the mouth of the flask. The acid was then evaporated to dryness on the water-bath and the residue was purified by dissolving in alkali, precipitating with hydrochloric acid and crystallizing from alcohol. This gave colorless needles, melting at 229°–230°. The solubility of the compound in alkali and its melting-point suggested that we had obtained the expected 1-phenyl-5-thiourazole, but our substance proved to be free from sulphur. Analysis:

	Calculated for $C_{14}H_{11}ON_3$.	Found.
N	17.72	17.79

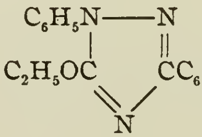
The result agreed with that calculated for a diphenyloxytriazole. 1,5-Diphenyl-3-oxytriazole melts at 288°–290°. The following synthesis proved, however, that our compound was the isomer or 1,3-diphenyl-5-oxytriazole.

Acetonephenylhydrazone and *benzoyl isocyanate* were slowly mixed in cold, dry benzene. Reaction took place at once, the solution was warmed for a few minutes and then, on cooling, a mass of crystals separated. On crystallizing several times from alcohol, colorless, microscopic, apparently hexagonal prisms were obtained. These melted, at about 139°–140°, to a clear, yellow oil which then turned red. A nitrogen determination agreed with that calculated for the semicarbazone, $C_6H_5CONHCON(C_6H_5).N : C(CH_3)_2$.

	Calculated for $C_{17}H_{17}O_2N_3$.	Found.
N	14.24	14.36

When this substance was warmed, for a few minutes, with dilute hydrochloric acid and then crystallized from alcohol fine, colorless needles were obtained, melting at 229°–230°. When these were mixed with the product of the hydrolysis of Wheeler and Dustin's compound, the melting-point was not altered. The two products were identical in every respect. 1,3-Diphenyl-5-oxytriazole is readily soluble in hot alcohol and only slightly soluble in boiling water, the solution having an acid reaction to litmus. It dissolves in ether and benzene.

1,3-Diphenyl-5-ethoxytriazole,

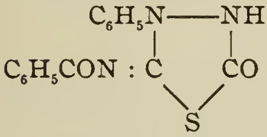


— Two grams of the above triazole and 0.6 gram of potassium hydroxide were dissolved in alcohol and an excess of ethyl bromide was added. The mixture was heated for 1 hour, at 100°. It was then evaporated and an oil was obtained which solidified when treated with water. On crystallizing from dilute alcohol shining, rhombic prisms separated, melting at 85°–86°. Analysis:

	Calculated for $C_{16}H_{15}ON_3$.	Found.
N	15.85	15.96

This material is readily soluble in alcohol, benzene and ether and it is slightly soluble in boiling water.

α′-Benzoylimino-β′-phenylthiobiazolon,



.—The compound described by Wheeler and Dustin, melting at 136°–138° (15 grams), was fused in an oil-bath, the temperature being kept at 140°–145° and hydrogen chloride was passed in for some time after the mass had solidified. The product was then extracted with hot, dilute alkali and filtered from unaltered material. It was precipitated with hydrochloric acid, washed and crystallized several times from alcohol, whereupon colorless needles were obtained melting, to a reddish-yellow oil, at 206°–207°. The yield was about 8 grams. Analysis:

	Calculated for $C_{15}H_{11}O_2N_3S$.	Found.
N	14.31	14.43

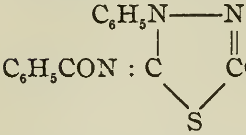
This material did not form an addition-product with ethyl iodide on standing in the cold. When boiled with strong alkali a portion was completely decomposed, the remainder being unaltered. It is slightly soluble in hot water, somewhat soluble in ether and benzene and readily soluble in boiling alcohol.

The *sodium salt* was not very readily soluble in cold alcohol. It was obtained by adding sodium ethylate to an alcoholic solution of the substance and it crystallized from alcohol in yellow needles, decomposing at about 240°.

The *silver salt* was prepared from the alcoholic solution of the sodium salt by adding the calculated quantity of silver nitrate, in dilute aqueous solution. It separated as a yellowish-white, amorphous precipitate, which was dried on a porous plate, then over sulphuric acid. Analysis:

	Calculated for $C_{15}H_{10}O_2N_3SAg$.	Found.
N	10.4	10.8

α-Ethoxy-α'-benzoylimino-β'-phenylbiazoline,



—The sodium salt described above does not react with ethyl bromide in the cold. α'-Benzoylimino-β'-phenylthiobiazolon (2 grams) was dissolved in the calculated amount of alcoholic sodium ethylate and heated with an excess of ethyl iodide, at 105°, for 2 hours. The contents of the tube were then evaporated and the residue, which consisted of unaltered biazolon and the ethoxy derivative, was purified by treating with alkali and crystallizing the insoluble material from alcohol. It then gave colorless or white prisms, melting at 137°–138° and, when mixed with the substance described by Wheeler and Dustin, the melting-point was not altered.

The same compound was formed when the silver salt of the biazolon was treated with ethyl iodide in the cold. When prepared by these methods the material is colorless. When obtained from benzoyl thiocyanate and ethyl phenylthioncarbazinate it is decidedly yellow at first and even upon repeated crystallization from alcohol it retains a yellowish tint. We also obtained this compound by the action of benzoyl isocyanchloride[1] on ethyl phenylthioncarbazinate, in chloroform.

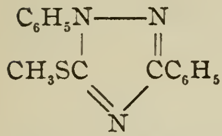
In the previous paper it was stated that an alcoholic solution of silver nitrate desulphurizes this material. It now appears that the action was due to a decomposition. Some of the substance was boiled in alcohol with moist mercuric oxide, for 18 hours. It was not desulphurized and unaltered material was obtained when it was heated, for 4 hours, with the freshly prepared oxide, in benzene, at 140°–150°.

The following derivatives of 1,3-diphenyl-5-thiotriazole were prepared in order to further characterize the substance. The isomeric 1,5-diphenyl-3-thiotriazole and the corresponding derivatives have been described by Wheeler and Beardsley.[2]

[1] Johnson and Menge: THIS JOURNAL, 32, 371 (1904).

[2] *Ibid.*, 27, 257 (1902).

1,3-Diphenyl-5-methylmercaptotriazole,



—1,3-Diphenyl-5-thiotriazole was first obtained by Wheeler and Beardsley from formyl phenyl hydrazine and benzoyl thiocyanate. It is best prepared by the method described by Johnson and Menge.[1]

Molecular proportions of 1,3-diphenyl-5-thiotriazole and sodium ethylate, in alcoholic solution, were treated with an excess of methyl iodide and allowed to stand 12 hours. The alcohol was then evaporated and the oil thus obtained was washed with water. On cooling, it solidified and when crystallized from alcohol it gave large, colorless needles, melting at 56°–57°, to a clear liquid. It is readily soluble in ether and benzene, insoluble in cold and sparingly soluble in boiling water. It dissolves readily in hot alcohol. Analysis:

	Calculated for $C_{15}H_{13}N_3S$.	Found.
N	15.73	15.90

1,3-Diphenyl-5-ethylmercaptotriazole.—This was prepared by acting on the sodium salt of the thiotriazole with ethyl bromide, in alcoholic solution, as described above. It formed colorless, stout prisms from alcohol and melted at 52°–53°. Analysis:

	Calculated for $C_{16}H_{15}N_3S$.	Found.
N	14.95	15.06

When dissolved in hydrobromic acid it gave a salt melting at 152°. On boiling, the material reverts to 1,3-diphenyl-5-thiotriazole.

1,3-Diphenyltriazole-5-disulphide, $(C_{14}H_{10}N_3)_2S_2$.—The thiotriazole was dissolved in the calculated quantity of sodium hydroxide and a slight excess of iodine was added. The whole was then evaporated to dryness and the residue was extracted with benzene when fine, colorless needles were obtained, melting at 182°–183°. The material was only slightly soluble in ether and alcohol and insoluble in water. Analysis:

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[1] This Journal, **32**, 369 (1904).

	Calculated for $(C_{14}H_{10}N_3S)_2$.	Found.
N	16.67	16.76

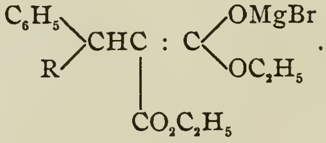
New Haven, Conn.,
March 3, 1905.

THE REACTION BETWEEN UNSATURATED COMPOUNDS AND ORGANIC MAGNESIUM COMPOUNDS.

VI. REACTIONS WITH ETHYL BENZALMALONATE.

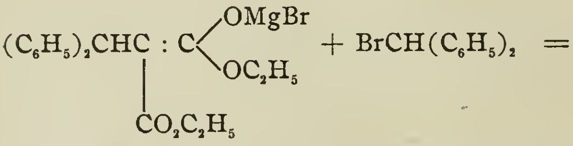
By E. P. Kohler.

A number of recent investigations have shown that alkylidene malonic esters have an unusual capacity for combining with dissimilar atoms or groups.[1] It was to be expected, therefore, that the first reaction between ethyl benzalmalonate and Grignard's reagent would consist in direct addition. I have found that this is the case and that the structure of the product is represented by the formula:



$$\begin{matrix} C_6H_5 \\ R \end{matrix}\!\!>CHC : C\!\!<\!\!\begin{matrix} OMgBr \\ OC_2H_5 \end{matrix}\;(\text{CHC}-CO_2C_2H_5).$$

This formula is based, mainly, on the reaction between the magnesium derivatives and diphenylbrommethane, which gives O-alkyl derivatives of substituted malonic esters. The product obtained with phenylmagnesium bromide, for example, reacts as follows:



$$(C_6H_5)_2CHC : C\!\!<\!\!\begin{matrix} OMgBr \\ OC_2H_5 \end{matrix}\;(\text{CHC}-CO_2C_2H_5) + BrCH(C_6H_5)_2 =$$

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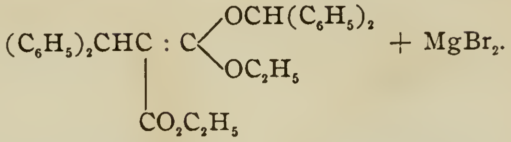
[1] Ann. Chem. (Liebig), **218**, 143; Ber. d. chem. Ges., **26**, 1877; Ann. Chem. (Liebig), **239**, 338; This Journal, **20**, 510; *Ibid.*, **31**, 243; Ann. Chem. (Liebig), **336**, 168.



It is difficult to introduce alkyl groups into substituted malonic esters that contain a branched chain and, occasionally, abnormal products are obtained in reactions with metallic derivatives of esters of this type; but, in the case under consideration, there is independent evidence that the magnesium compound has the same structure as the O-alkyl derivative. The latter, like the corresponding nitrile described in a previous paper, is an extremely unreactive substance—the carbethoxyl does not react with Grignard's reagent and it even resists saponification by the methods commonly used for this purpose. The inertness is evidently connected with its peculiar structure, since it is common to all the substances of this type that I have obtained.

The magnesium compound shows this same lack of activity, its carbethoxyl group is not attacked by organic magnesium compounds, although, as was shown by Valeur,[1] this reagent replaces both of the groups of malonic ester.

The reactions described in this paper can be used for preparing substituted malonic acids that are not easily made by other methods. The esters obtained by decomposing the magnesium compounds boil without decomposing and they are easily hydrolyzed to the corresponding acids, hence the yield of the latter is excellent. These reactions can also be used for preparing α,β-unsaturated acids, but in this case the yield is affected by the instability of some of the intermediate compounds.

EXPERIMENTAL.

The reaction between ethyl benzalmalonate and organic magnesium compounds is not affected by the relative amounts of the substances or the conditions under which they are brought together. This conclusion is based on the following preliminary experiments:

[1] Compt. rend., **132**, 833.

see errata p. 625

Two solutions of methyl magnesium iodide, each containing 1 gram equivalent of magnesium, were made in the usual way and cooled in a freezing-mixture. An ethereal solution, containing half the calculated amount of ethyl benzalmalonate, was slowly added to the one, while the other was siphoned, drop by drop, into a similar solution containing twice the calculated amount of ester. After the liquids had remained in a freezing-mixture for several hours, portions of each were removed with a pipette and decomposed with ice-water. The remainders were boiled for 8 hours and then also poured into ice-water. The product was the same in all cases. The following procedure was, therefore, used in all subsequent experiments. An ethereal solution of the ester (1 mol.) was added, gradually, to a solution of the magnesium compound (1 mol.), cooled in ice-water. The resulting liquid was boiled for half an hour and then treated with the various reagents used. The magnesium derivative itself was not isolated.

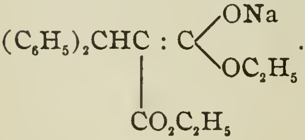
Ethyl Diphenylmethylmalonate, $(C_6H_5)_2CHCH(CO_2C_2H_5)_2$.—The solution of the magnesium compound was poured into ice-water, the ethereal layer washed with water, dried with sodium sulphate and distilled under diminished pressure. The fraction boiling at 235°–250° (12 mm.) solidified in a freezing-mixture. After one crystallization from low-boiling ligroin the solid melted sharply at 63°. Analysis:

0.1540 gram substance gave 0.4248 gram CO_2 and 0.0963 gram H_2O.

	Calculated for $C_{20}H_{22}O_4$.	Found.
C	73.62	73.51
H	6.74	6.89

The ester separates from ligroin in fine needles. It is readily soluble in alcohol, ether, and carbon bisulphide; moderately in low-boiling ligroin. The yield was excellent: 27 grams from 25 grams of ethyl benzalmalonate.

Sodium Ethyl Diphenylmethylmalonate,



$$(C_6H_5)_2CHC(CO_2C_2H_5) : C\begin{cases} ONa \\ OC_2H_5 \end{cases}$$

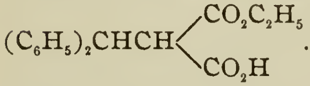
.—Ethyl diphenylmethylmalonate is

insoluble in alkalies and it gives no color reaction with ethereal solution of ferric chloride, but in ethereal solution it readily dissolves sodium, with evolution of hydrogen. The sodium derivative is soluble in ether, hence the surface of the metal remains clean and the action continues until the solution contains 1 atom of sodium per molecule of ester. The ether, on evaporation in a current of carefully dried air, deposits the sodium derivative in small, white needles. Analysis:

0.2112 gram substance gave 0.0428 gram Na_2SO_4.

	Calculated for $C_{20}H_{21}O_4Na$.	Found.
Na	6.61	6.55

Monoethyl Diphenylmethylmalonate,



$(C_6H_5)_2CHCH\begin{cases}CO_2C_2H_5\\CO_2H\end{cases}$.—It is easy to hydrolyze ethyl diphenylmethylmalonate in steps. To get the ester acid an alcoholic solution of 1 molecule of ester and 1 of potassium hydroxide was allowed to remain, at the ordinary temperature, until the reaction was neutral to litmus. The solution was clear, but ether precipitated a potassium salt in fine, white needles. This was filtered, washed with ether and dissolved in water. On acidifying this solution the acid was precipitated as a crystalline solid. It was purified by recrystallization from alcohol. Analysis:

0.1511 gram substance gave 0.4005 gram CO_2 and 0.0857 gram H_2O.

	Calculated for $C_{18}H_{18}O_4$.	Found.
C	72.50	72.29
H	6.04	6.28

The acid is deposited in thick needles that melt at 165°–166° and give off carbon dioxide above 220°. It is readily soluble in ether and acetone, moderately in alcohol and sparingly in ligroin and in boiling water.

Diphenylmethylmalonic Acid, $(C_6H_5)_2CHCH_2(CO_2H)_2$.—Excess of strong, aqueous potassium hydroxide was added to an alcoholic solution of the ester. The liquid became hot and in a short time a potassium salt began to separate in long, colorless needles. The salt was filtered and washed with absolute alcohol. From its aqueous solution hydrochloric acid precipitated an oil that soon solidified. The solid was purified by recrystallization from hot water. Analysis:

0.1926 gram substance gave 0.5022 gram CO_2 and 0.0915 gram H_2O.

	Calculated for $C_{16}H_{14}O_4$.	Found.
C	71.11	71.06
H	5.18	5.28

Diphenylmethylmalonic acid is readily soluble in alcohol and ether, moderately in hot water, very slightly in cold water. In boiling water it slowly loses carbon dioxide and passes into β,β-diphenylpropionic acid. It separates from water in thin plates and from alcohol in needles. It melts, with decomposition, at 190°–192°.

Ethyl Bromdiphenylmethylmalonate, $(C_6H_5)_2CHCBr(CO_2C_2H_5)_2$. — Bromine, that had been carefully dried by distillation from phosphorus pentoxide, was dropped into an ethereal solution of the magnesium derivative, obtained from 5 grams of magnesium, 34 grams of brombenzene and 32 grams of ethyl benzalmalonate. The reaction was so energetic that it was necessary to cool in a freezing-mixture. As soon as the color of bromine no longer disappeared on shaking, the mixture was poured into ice-water and the product isolated in the usual way. It was purified by crystallization from alcohol. Analysis:

0.1669 gram substance gave 0.3629 gram CO_2 and 0.0776 gram H_2O.

	Calculated for $C_{20}H_{21}O_4Br$.	Found.
C	59.26	59.19
H	5.15	5.16

The substance is readily soluble in acetone and ether, moderately in alcohol, sparingly in ligroin, From alcohol it separates in large, diamond-shaped plates, melting at 79°–80°.

Hydrolysis of Ethyl Bromdiphenylmethylmalonate.—I did not succeed in getting the dibasic acid. When an alcoholic solution of the ester and one equivalent of potassium hydroxide is kept in an ice chest, for several days, it usually deposits a mixture of potassium carbonate and the potassium salt of a brom-organic acid. The latter salt is extremely unstable, but it can be purified by dissolving it in the smallest possible quantity of water, at the ordinary temperature, adding a little alcohol and cooling this solution in ice-water. The pure salt forms a clear solution in ice-water. It separates from water in colorless needles. Analysis:

0.2346 gram substance gave 0.0535 gram K_2SO_4.

	Calculated for $C_{15}H_{12}O_2BrK.2H_2O$.	Found.
K	10.50	10.24

The analysis and the transformations described below show that this is potassium α-brom-β,β-diphenylpropionate formed according to the equation:

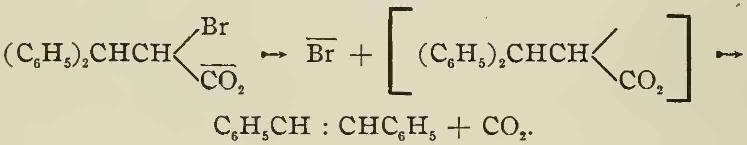
$$(C_6H_5)_2CHCBr(CO_2C_2H_5)_2 + 3KOH = \\ (C_6H_5)_2CHCHBrCO_2K + 2C_2H_5OH + K_2CO_3.$$

At 130° the salt begins to lose water, but it also undergoes partial decomposition and the residue is no longer completely soluble in water. The same change takes place in water solution. Bromine ions can be detected in a dilute solution in ice-water a short time after it is made and, if such a solution be allowed to stand, it soon becomes turbid. The change, of course, takes place much more rapidly on warming. To determine the nature of the products a solution of 5 grams of the salt, in 100 grams of water, was boiled, for an hour, in a flask connected with an inverted condenser. The liquid was then cooled and extracted with ether. The ether, on evaporation, deposited 2.1 grams of a crystalline solid that melted at 124° and gave a bromine addition-product melting at 237°. This was stilbene. The aqueous solution, on evaporation, left potassium bromide, free from organic matter; the salt had, therefore, decomposed completely into stilbene, carbon dioxide and potassium bromide.

This remarkable change is essentially like that described by Elbs and Förster.[1] These investigators found that the polyhalogen derivatives of unsymmetrical diarylethanes regularly give stilbenes on reduction. On treating diphenyltrichlorethane, for example, with zinc dust and alcohol, they obtained stilbene itself:

$$(C_6H_5)_2CHCCl_3 \rightarrow C_6H_5CH{=}CHC_6H_5 + ZnCl_2.$$

In the case of potassium diphenylbrompropionate the result is evidently due to an ion reaction, since the change takes place in dilute aqueous solution and proceeds more rapidly in solutions of the sodium or potassium salts than in those of the free acid. It may be represented as follows:



$$(C_6H_5)_2CHCH\left\langle\begin{matrix}Br\\ \overline{CO_2}\end{matrix}\right. \rightarrow \overline{Br} + \left[(C_6H_5)_2CHCH\left\langle\begin{matrix}\\ CO_2\end{matrix}\right.\right] \rightarrow$$
$$C_6H_5CH : CHC_6H_5 + CO_2.$$

It would be interesting to compare this result with some others that have been obtained by the action of bromine on aqueous solutions of salts; but as I am now studying this subject by kinetic methods I shall defer the discussion to a later paper.

The following experiment shows that, although potassium diphenylbrompropionate easily breaks down into simpler substances, it is, nevertheless, possible to eliminate hydrobromic acid and get β-phenylcinnamic acid without serious loss of material. Ten grams of the salt were added, in small quantities, to excess of potassium hydroxide in boiling, absolute alcohol. After boiling for an hour most of the alcohol was distilled, the residue poured into water and the milky solution extracted with ether. The ethereal solution, on evaporation, deposited less than 0.5 gram of stilbene, while the aqueous solution, when acidified, gave 4.55 grams of pure phenylcinnamic acid, melting at 158°, a yield of 80 per cent.

A fairly good yield of β-phenylcinnamic acid may also be obtained by adding ethyl bromdiphenylmethylmalonate, in small quantities, to strong, boiling, alcoholic potassium hydroxide; 22 grams of ester gave 8 grams of the unsaturated acid, a yield of 72 per cent.

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[1] J. prakt. Chem., [2], 39, 45.

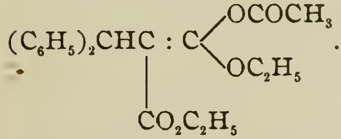
α-Brom-β,β-diphenylpropionic Acid, $(C_6H_5)_2CHCHBrCO_2H$. —The pure acid was obtained by acidifying a solution of the pure potassium salt and recrystallizing the precipitate from a mixture of chloroform and ligroin. Analysis:

0.1342 gram substance gave 0.2920 gram CO_2 and 0.0480 gram H_2O.

	Calculated for $C_{15}H_{13}O_2Br$.	Found.
C	59.01	59.30
H	4.25	4.05

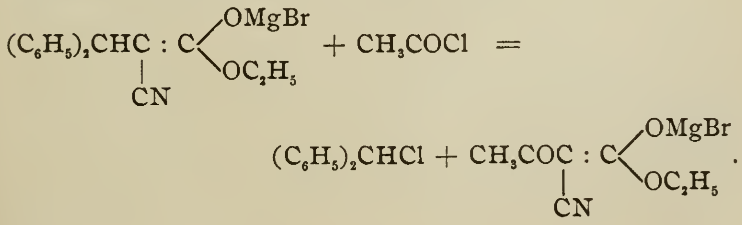
The acid is sparingly soluble in water; the solution changes much more slowly than those of its salts, but the acid ultimately decomposes completely into carbon dioxide, hydrobromic acid and stilbene.

Ethyl O-Acetyldiphenylmethylmalonate,



$$(C_6H_5)_2CH\underset{\underset{\displaystyle CO_2C_2H_5}{|}}{C} : C\left\langle\begin{matrix}OCOCH_3\\ OC_2H_5\end{matrix}\right.$$

.—In earlier papers it was shown that the reaction between acyl chlorides and the magnesium derivatives, formed by adding Grignard's reagent to unsaturated compounds, usually results in the replacement of the magnesium halide residue with an acyl group — the product being an O-acyl derivative. The magnesium compounds obtained from ethyl α-cyancinnamate, however, behave quite differently; the carbon chain is broken and the result is a magnesium derivative of a β-ketonic ester:



$$(C_6H_5)_2CH\underset{\underset{\displaystyle CN}{|}}{C} : C\left\langle\begin{matrix}OMgBr\\ OC_2H_5\end{matrix}\right. + CH_3COCl =$$

$$(C_6H_5)_2CHCl + CH_3CO\underset{\underset{\displaystyle CN}{|}}{C} : C\left\langle\begin{matrix}OMgBr\\ OC_2H_5\end{matrix}\right. .$$

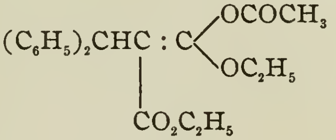
It was, therefore, of interest to ascertain whether the magnesium derivatives obtained from ethyl benzalmalonate would behave normally, or like those obtained from the corresponding nitrile. The former was found to be the case. Acetyl chloride, in slight excess, was added to the ethereal solution of the magnesium derivative, the mixture boiled for half an hour and poured into iced hydrochloric acid. The ethereal layer, on evaporation, deposited a crystalline solid and a small quantity of oil. The oil was drawn off with the pump, the crystals washed with a small quantity of cold ether and recrystallized from alcohol. Analysis:

0.1991 gram substance gave 0.5227 gram CO_2 and 0.1220 gram H_2O.

	Calculated for $C_{22}H_{24}O_5$.	Found.
C	71.74	71.65
H	6.52	6.69

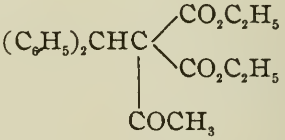
The substance is readily soluble in chloroform, acetone and boiling alcohol; moderately in boiling ether; very slightly in low-boiling ligroin. It is deposited from alcohol in large, lustrous plates, melting at 92°.

It is extremely difficult to distinguish between the two possible formulas for this acetyl derivative:



$(C_6H_5)_2CH\underset{\underset{\displaystyle CO_2C_2H_5}{|}}{C} : C\Big\langle\begin{array}{l}OCOCH_3\\OC_2H_5\end{array}$

I.



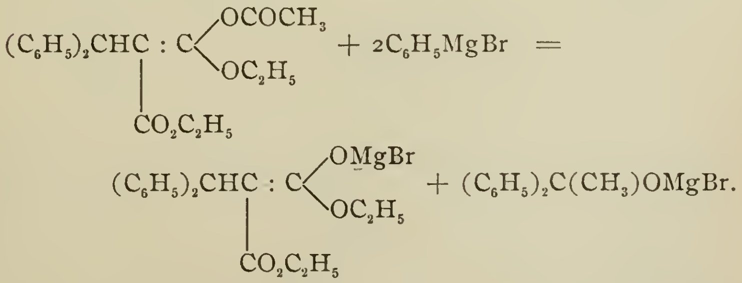
$(C_6H_5)_2CH\underset{\underset{\displaystyle COCH_3}{|}}{C}\Big\langle\begin{array}{l}CO_2C_2H_5\\CO_2C_2H_5\end{array}$

II.

Each of them represents a substance that would be incapable of forming metallic derivatives and indifferent to ferric chloride. A compound with the structure represented by I. would, on hydrolysis, necessarily give a substituted malonic acid; but some C-acyl derivatives of malonic ester are hydrolyzed in the same way. Phenacetylmalonic ester, for example, yields phenylacetic and malonic acids when saponified with bases. With dilute sulphuric acid its ester gives methyl benzyl ketone, but this method of hydrolysis has been applied to so few esters of the kind that the result cannot be used as a basis for determining the structure of an unknown substance.

The acetyl derivative in question is hydrolyzed with the greatest ease. When it is allowed to stand, in alcoholic solution, with exactly one equivalent of sodium ethylate, the products are ethyl acetate and the same sodium derivative of ethyl diphenylmethylmalonate that is formed by the direct action of sodium on the ester. When the acetyl derivative is treated with one equivalent of alcoholic potassium hydroxide the principal products are potassium acetate and ethyl diphenylmethylmalonate, but the reaction always proceeds further, some of the ester being transformed into the ester salt previously described. With excess of boiling, alcoholic potassium hydroxide, the change into potassium acetate and potassium diphenylmethylmalonate is quantitative.

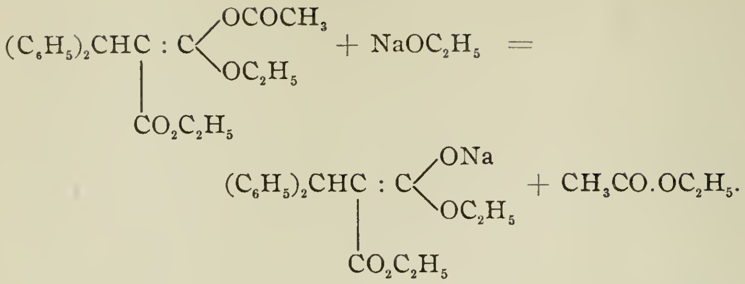
The most significant results are, probably, those obtained with Grignard's reagent. The acetyl derivative was added to an ethereal solution of phenyl magnesium bromide and the mixture boiled for several hours. The products, isolated in the usual way, were ethyl diphenylmethylmalonate and methyldiphenylcarbinol, melting at 98°. The reaction is represented by the following equation :



$$\underset{\textstyle CO_2C_2H_5}{(C_6H_5)_2CHC} : C\left\langle\begin{matrix}OCOCH_3\\OC_2H_5\end{matrix}\right. + 2C_6H_5MgBr =$$

$$\underset{\textstyle CO_2C_2H_5}{(C_6H_5)_2CHC} : C\left\langle\begin{matrix}OMgBr\\OC_2H_5\end{matrix}\right. + (C_6H_5)_2C(CH_3)OMgBr.$$

It is hardly conceivable that such a reaction could take place with a compound that has the structure represented by II. I therefore regard the substance as an O-acetyl derivative. This is in harmony with its behavior towards sodium ethylate :



$$(C_6H_5)_2\underset{\begin{array}{c}|\\ CO_2C_2H_5\end{array}}{CHC} : C\Big\langle{OCOCH_3 \atop OC_2H_5} + NaOC_2H_5 =$$

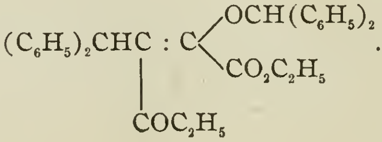
$$(C_6H_5)_2\underset{\begin{array}{c}|\\ CO_2C_2H_5\end{array}}{CHC} : C\Big\langle{ONa \atop OC_2H_5} + CH_3CO.OC_2H_5.$$

The oil that is formed along with the solid just described contains a second acetyl derivative. This could not be obtained in perfectly pure condition, because even the purest specimen did not solidify in a freezing-mixture and decomposed when distilled under greatly diminished pressure. The purest specimen was obtained as follows: An ethereal solution of the crude oil was washed with dilute sodium carbonate, dried over sodium sulphate and the ether evaporated in a current of dry air. The residue was repeatedly extracted with low-boiling ligroin, the first extract being discarded. The colorless oil, left after evaporating the ligroin, was heated at 150°, in a current of dry carbon dioxide, under 15 mm. pressure. The residue was analyzed:

0.1810 gram substance gave 0.4780 gram CO_2 and 0.1092 gram H_2O.

	Calculated for $C_{22}H_{24}O_5$.	Found.
C	71.74	72.00
H	6.52	6.70

The chemical properties of this substance are exactly the same as those of the solid acetyl derivative. It even gives the same products with phenylmagnesium bromide. It therefore seems to be a geometrical isomer of the solid, but I have not succeeded in transforming either of these substances into the other.



$$(C_6H_5)_2\underset{\begin{array}{c}|\\ COC_2H_5\end{array}}{CHC} : C\Big\langle{OCH(C_6H_5)_2 \atop CO_2C_2H_5}.$$

The magnesium derivatives obtained from ethyl benzalmalonate do not react with simple alkyl haloids. Ethereal solutions of several of these substances were boiled for hours with methyl iodide, isopropyl bromide, allyl iodide, tertiary butyl bromide and ethyl brommalonate, but in each case the alkyl haloid remained unchanged. With the unusually reactive diphenylbrommethane, however, a reaction takes place even at the ordinary temperature and the product is an O-alkyl derivative. Twelve grams of the haloid were added to an ethereal solution, obtained from 12 grams of ethyl benzalmalonate and the equivalent amount of phenylmagnesium bromide. The reaction started at once, the heat developed raising the temperature of the liquid to the boiling-point. The solution was boiled for 3 hours, then poured into ice-water. The ethereal layer, on evaporation, left a solid which was recrystallized from absolute alcohol. The substance was deposited in plates, melting at 132°. It is readily soluble in chloroform and acetone, moderately in alcohol and ether. Analysis:

I. 0.1797 gram substance gave 0.5297 gram CO_2 and 0.1050 gram H_2O.

II. 0.1623 gram substance gave 0.4822 gram CO_2 and 0.0941 gram H_2O.

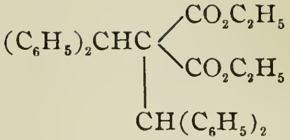
	Calculated for $C_{33}H_{32}O_4$.	Found.	
		I.	II.
C	80.48	80.39	80.55
H	6.50	6.49	6.40

Molecular Weight Determined in Boiling Acetone.

K = 1710.

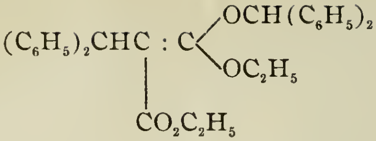
Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
52.00	0.6125	0.042	479
	1.1510	0.082	502
	1.9010	0.129	483
		Calculated for $C_{33}H_{32}O_4$,	492

It is easy to decide between the two possible formulas for this substance;



$$(C_6H_5)_2CH\underset{\displaystyle CH(C_6H_5)_2}{C}\begin{matrix}\diagup CO_2C_2H_5\\ \diagdown CO_2C_2H_5\end{matrix}$$

I.



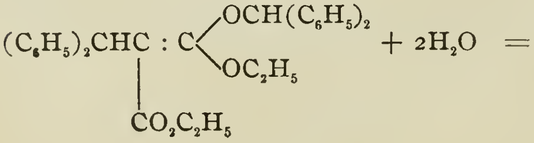
$$(C_6H_5)_2CH\underset{\displaystyle CO_2C_2H_5}{C} : C\begin{matrix}\diagup OCH(C_6H_5)_2\\ \diagdown OC_2H_5\end{matrix}$$

II.

If the substance were a C-alkyl derivative (I.) it should be easy to hydrolyze it to the corresponding acid or, at any rate, to transform it into an acid containing two diphenylmethyl groups. This is impossible. Boiling, alcoholic potassium hydroxide and boiling, dilute sulphuric acid (1 : 3) have no effect on the substance. It can be decomposed by heating at 150°–160° with alcoholic potassium hydroxide, but one of the diphenylmethyl groups is eliminated. The same result was obtained when the substance was heated, at 175°, with concentrated hydrochloric acid and the reaction was much cleaner, so that all the products could be isolated.

Twenty-five grams of the substance were sealed up with fuming hydrochloric acid and heated, at 175°–180°, for 8 hours. A considerable pressure in the tube was found to be due to carbon dioxide and ethyl chloride. The tube was emptied into water and the organic substances dissolved in ether. From the ethereal solution sodium carbonate extracted β,β-diphenylpropionic acid—the only organic acid found. The ethereal solution, left after extraction with sodium carbonate, was dried, the ether evaporated and the residue distilled. Almost the entire amount distilled at 210°, the boiling-point of diphenylmethylethyl ether. The boiling-point remained unchanged when the distillate was mixed with its own volume of this ether, made directly from diphenylbrommethane.

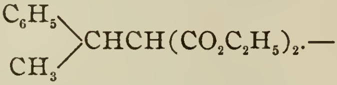
The original substance is evidently an O-alkyl derivative of ethyl diphenylmethylmalonate (II.). When heated with concentrated hydrochloric acid it breaks down at the double linkage :



$$(C_6H_5)_2CH\underset{\displaystyle CO_2C_2H_5}{C} : C\begin{matrix}\diagup OCH(C_6H_5)_2\\ \diagdown OC_2H_5\end{matrix} + 2H_2O =$$

$$(C_6H_5)_2CHCH_2CO_2H + CO_2 + C_2H_5OH + (C_6H_5)_2CHOC_2H_5.$$

Ethyl β-Phenylethylmalonate,



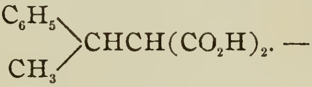
$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} \Big> CHCH(CO_2C_2H_5)_2.$$

—This compound was obtained by adding methylmagnesium iodide to ethyl benzalmalonate, decomposing the magnesium derivative with dilute acid and fractionating the product under diminished pressure. It is a colorless liquid that boils at 230°–235° (15 mm.). Analysis:

0.1442 gram substance gave 0.3590 gram CO_2 and 0.1001 gram H_2O.

	Calculated for $C_{15}H_{20}O_4$.	Found.
C	68.14	67.89
H	7.50	7.71

β-Phenylethylmalonic Acid,



$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} \Big> CHCH(CO_2H)_2.$$

—The potassium salt of the acid separated in needles when concentrated, aqueous potassium hydroxide was added to an alcoholic solution of the ester. The acid was recrystallized from hot water, which deposits it in large plates. Analysis:

0.1892 gram substance gave 0.4405 gram CO_2 and 0.1021 gram H_2O.

	Calculated for $C_{11}H_{12}O_4$.	Found.
C	63.46	63.49
H	5.80	5.98

Phenylethylmalonic acid is readily soluble in alcohol and ether, moderately in boiling water, sparingly in cold water and in ligroin. It melts at 144°. Above 170° it loses carbon dioxide rapidly. The colorless oil, left after heating several grams of the acid, at 180°, until there was no further gas evolution, solidified in the course of a week and could then be recrystallized from low-boiling ligroin. It was obtained in large, lustrous prisms, melting at 47°. Analysis:

0.1812 gram substance gave 0.4850 gram CO_2 and 0.1224 gram H_2O.

	Calculated for $C_{10}H_{12}O_2$.	Found.
C	73.11	72.94
H	7.30	7.51

The substance is evidently β-phenylbutyric acid. An acid of this composition and structure was described in a previous paper[1] as an oil. The specimen left over from the earlier experiments solidified completely when brought in contact with a crystal of the new preparation.

α-Brom-β,β-methylphenylbutyric Acid,

$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} \!\! > CH_2\overset{\beta}{C}H\overset{\alpha}{C}HBrCO_2H$.—This acid was made for the purpose of ascertaining whether substances of the type of bromdiphenylpropionic acid also undergo rearrangement into ethylene derivatives, when one of the hydrocarbon residues is aliphatic. One equivalent of ethyl benzalmalonate was added to an ethereal solution of ethylmagnesium bromide and the mixture boiled for an hour. The liquid was then cooled in a freezing-mixture and bromine added, drop by drop, until the color no longer disappeared on shaking. The mixture was poured into ice-water, the ethereal layer dried with sodium sulphate and the ether evaporated in a current of dry air. The pale-yellow oil that remained was cooled in a freezing-mixture and treated with a concentrated alcoholic solution of potassium hydroxide, containing a little less than one equivalent of the base. In the course of a few hours a potassium salt separated in long, silky needles. The salt gave no consistent analytical results and it could not be recrystallized from water or alcohol. From its solution in ice-water, hydrobromic acid precipitated a solid that could be purified by recrystallization from a mixture of chloroform and ligroin. Analysis:

0.2260 gram substance gave 0.4272 gram CO_2 and 0.0836 gram H_2O.

	Calculated for $C_{11}H_{13}O_2Br$.	Found.
C	51.32	51.54
H	4.40	4.18

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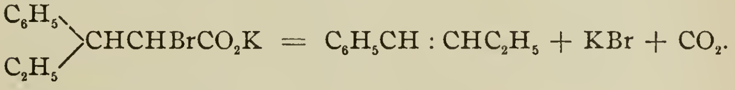
[1] This Journal, 33, 353.

α-Brom-β,β-methylphenylbutyric acid is readily soluble in alcohol, ether and chloroform, very slightly in water and ligroin. It melts at 176° and decomposes above 190°. A clear, aqueous solution of its potassium salt soon becomes milky, even at 0°. The aqueous solution of the acid is more stable, but it also becomes milky on standing.

An aqueous solution of the potassium salt was distilled with steam and the oily distillate extracted with ether. After drying the ethereal solution over calcium chloride, the ether was evaporated and the residue distilled. The temperature rose rapidly to 184° and the entire product passed over between 184° and 186°. A small quantity of the oil was treated with the calculated amount of bromine, dissolved in chloroform. The latter, on evaporation, left a solid which, after one recrystallization from ligroin, melted at 70°–71°. The oil is phenylbutylene, which boils at 186° and forms a bromine addition-product melting at 70°. It is evident, therefore, that the salts of this type decompose exactly like those of bromdiphenylpropionic acid:



$$\left.\begin{matrix}C_6H_5\\C_2H_5\end{matrix}\right>CHCHBrCO_2K = C_6H_5CH:CHC_2H_5 + KBr + CO_2.$$

Chemical Laboratory,
Bryn Mawr College,
March, 1905.

THE ACID OXALATES OF AMMONIUM.

By P. T. Walden.

The work described in this paper was undertaken for the purpose of supplementing that of Foote and Andrew[1] on "The Acid Oxalates of Lithium, Sodium, Potassium and Caesium."

The experimental method used is that devised by Foote[2] and depends upon the principle that two simple salts with a common ion, when mixed in varying proportions and dissolved, will separate, at a fixed temperature, solid residues of a varying composition and leave solutions of a constant composition, except where a double salt forms. In this case the residue will be constant and the solution variable. The term salt is here used in the broad sense which includes all electrolytes, acid salts are, in this sense, double salts of hydrogen and metal.

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[1] This Journal, **34**, 153.

[2] *Ibid.*, **30**, 330.

The acid oxalates described in this paper are the only ones that can be prepared from mixtures of ammonium oxalate and oxalic acid, in water solution, at 25°. This statement is warranted by the experimental method employed and the principle which underlies it.

The compound, $(NH_4)_2C_2O_4.H_2C_2O_4.2H_2O$, described by Rammelsberg,[1] I have been unable to prepare, but I have obtained both the acid salts which Nichols[2] describes,

$$(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O \text{ and } (NH_4)_2C_2O_4.H_2C_2O_4.H_2O.$$

It is interesting to notice that in Ladenburg's "Handwörterbuch der Chemie" (1890) and in Beilstein (1893) Rammelsberg's formula for the 1 : 1 salt is retained, while Roscoe and Schorlemmer (1884) give only Nichols' formula for this salt.

In carrying out each experiment enough of the mixture of ammonium oxalate and oxalic acid was dissolved, in about 15 cc. of hot water, to make a solution that would crystallize when cooled. This was put in a thermostat, kept at 25° and constantly shaken for at least 48 hours. Samples of the solid residue and of the solution were then taken out and analyzed for ammonium oxalate and for oxalic acid. Twenty different mixtures were prepared and examined before it was evident that all the essential conditions had been covered. The proportion of salt to acid varied from almost pure ammonium oxalate at one end to almost pure oxalic acid at the other.

The samples for analysis were boiled with potassium hydroxide to expel ammonia, which was absorbed in standard hydrochloric acid solution and this was then titrated with standard ammonium hydroxide. Total oxalate was determined by titration with permanganate and the per cent of free oxalic acid calculated from these values.

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[1] Pogg. Ann., **93**, 24 (1854).

[2] Chem. News, **22**, 14 (1870).

The analytical results for solutions and residues are shown below. Italics indicate analyses of pure acid salts :

	Per cent of $(NH_4)_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in solution.	Per cent of $(NH_4)_2C_2O_4$ in residue.	Per cent of $H_2C_2O_4$ in residue.
1	0.22	10.30	6.12	68.05
2	0.35	10.00	12.39	64.96
3	0.28	10.30	25.32	57.68
4	0.46	7.24	*26.32*	*57.57*
5	2.44	2.59	*26.58*	*57.72*
6	3.65	2.80	*26.82*	*57.67*
7	4.99	3.41	*27.03*	*57.51*
8	5.20	3.64	31.90	54.08
9	5.25	3.49	41.55	47.12
10	5.24	3.51	48.36	41.83
11	5.04	3.61	52.48	39.44
12	5.36	3.38	*53.37*	*38.53*
13	6.27	3.04	*53.18*	*37.71*
14	7.03	2.90	*53.26*	*38.94*
15	7.22	2.90	57.18	33.95
16	7.12	2.89	70.95	18.25
17	7.15	2.88	74.55	14.80
18	7.17	2.73	75.55	13.14
19	6.91	2.11	77.38	11.10
20	6.92	2.31	86.62	0.00
Calculated for $(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$			26.61	57.94
Calculated for $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$			53.45	38.79

It will be seen, from the above table, that mixtures 4, 5, 6 and 7, on the one hand and 12, 13 and 14, on the other, crystallized out solids, at 25°, which were found to be almost constant in composition, while the solutions from which they came showed a steadily varying proportion of components. Evidently, then, we have only two acid ammonium oxalates capable of existence at this temperature, *viz.* :

$(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$ and $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$.

The theoretical composition of these salts, as it is given below the table, is seen to agree, approximately, with the results obtained by analyzing the solid residues from those solutions the composition of which varied (4, 5, 6 and 7 and 12, 13, and 14).

The same result is shown, graphically, in Fig. I., where the percentages of oxalic acid in solution are plotted as ordinate and those in the residue as abscissa.

Because of the very slight variation in the composition of the solutions from which the salt $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$ forms, it was thought that conditions might be found, by changing the temperature, where this salt would decompose into ammonium oxalate and the 3 : 1 acid salt, according to the equation:

$$3(NH_4)_2C_2O_4.H_2C_2O_4.H_2O + 3H_2O = 2(NH_4)_2C_2O_4.H_2O + (NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O.$$

Such a change would make itself evident by an irregular change of volume at the inversion temperature and this temperature can readily be found by the use of a dilatometer.[1]

Accordingly, some of this salt was prepared, mixed with a little ammonium oxalate, moistened with its mother-liquor and placed in a dilatometer, which was then filled with toluene to register the change of volume. This was subjected to a gradual rise of temperature, between its cryohydric temperature (about —4°) at one end and 70° at the other. A gradual and regular change of volume only was observed. It was, therefore, concluded that the 1 : 1 salt is stable through this range of temperature conditions and the attempt to decompose it was abandoned.

By a simple calculation from the table of solubilities, given above, we can ascertain whether or not the acid oxalates here described can be recrystallized from water. Evidently, if a double or acid salt can be recrystallized from water, it should be capable of forming from a solution containing the same relative quantities of the constituent simple salts present in the double one.

$(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$ contains 26.61 parts of $(NH_4)_2C_2O_4$: 57.94 parts of $H_2C_2O_4$.

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[1] Van 't Hoff: "Vorles. über Bild. u. spalt. von. Doppelsalzen."

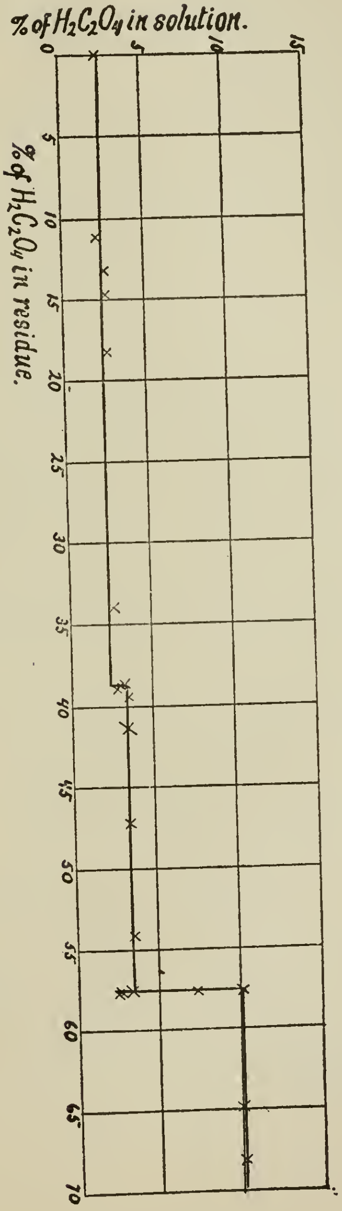
% of $H_2C_2O_4$ in solution.
0
5
10
15
% of $H_2C_2O_4$ in residue.
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70

Fig. I.

We find, from the table, that the solutions from which this salt was obtained consist of 46 parts of $(NH_4)_2C_2O_4$: 724 parts of $H_2C_2O_4$ in solution 4 and 499 parts of $(NH_4)_2C_2O_4$: 341 parts of $H_2C_2O_4$ in solution 7.

Calculating these proportions to correspond to the percentages of the acid salt above, we have: 26.61 parts of $(NH_4)_2C_2O_4$: 418.80 parts of $H_2C_2O_4$ in solution 4 and 26.61 parts of $(NH_4)_2C_2O_4$: 18.19 parts of $H_2C_2O_4$ in solution 7.

It will be seen that the composition of the acid salt falls within these limits and, therefore, it can be recrystallized from water.

Calculating, in the same way, for the salt $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$ we find the composition of the solutions from which it forms to be 53.45 parts of $(NH_4)_2C_2O_4$: 33.70 parts of $H_2C_2O_4$ in solution 12 and 53.45 parts of $(NH_4)_2C_2O_4$: 22.05 parts of $H_2C_2O_4$ in solution 14.

The composition of the 1 : 1 acid salt is 53.45 parts of $(NH_4)_2C_2O_4$: 38.79 parts of $H_2C_2O_4$. Therefore this salt is not susceptible of recrystallization.

An experimental verification of this point was made by preparing crops of the two acid salts, crystallizing them from water at 25° and analyzing the substances obtained. The results are given below:

	Calculated for $(NH_4)_2C_2O_4.3H_2C_2O_4.4H_2O$.	Found for salt made from simple salts.		Found for recrystallized salt.	
		A.	B.	A.	B.
$(NH_4)_2C_2O_4$	26.61	27.24	27.21	26.33	. .
$H_2C_2O_4$	57.94	57.49	57.57	58.11	58.04
H_2O	15.45	. .	. .	. .	. .

	Calculated for $(NH_4)_2C_2O_4.H_2C_2O_4.H_2O$.	Found for salt made from simple salts.		Found for recrystallized salt.
		A.	B.	A.
$(NH_4)_2C_2O_4$	53.45	52.95	53.01	25.60
$H_2C_2O_4$	38.79	38.85	38.94	56.53
H_2O	7.76	. .	. .	. .

SHEFFIELD LABORATORY,
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March, 1905.

THE ACID OXALATES OF LITHIUM, SODIUM, POTASSIUM AND CAESIUM AND THEIR SOLUBILITY.

By H. W. Foote and I. A. Andrew.

The acid oxalates of lithium, sodium, potassium and caesium have been investigated by the same method used by Walden in the preceding article, the object being to determine all the stable acid salts capable of forming at 25° and the solubility conditions under which they form. The method depends on the principle that, when the components of the acid salts are mixed in varying proportions and treated with water at a constant temperature, the residue remains constant in composition and the solution varies if a pure acid oxalate is present, while, on the other hand, the residue varies and the solution remains constant in composition when a mixture of two oxalates is present. The mixtures were prepared and treated as in the preceding article. Both solutions and residues were analyzed. In the analysis, oxalic acid was determined by titrating with standard sodium hydroxide and total oxalate by titration with potassium permanganate. The amount of alkali oxalate could then be calculated.

The tabulated results which follow are divided into groups, each group representing either (1) constant solubility and varying residue, corresponding to a mixture of salts, or (2) varying solubility and constant residue corresponding to a pure double salt. The residues which are constant, showing pure double salt, are italicized. The solubility of oxalic acid and of the alkali oxalates alone is also given. All the results are for 25°.

1. Oxalic Acid and Lithium Oxalate.

Rammelsberg[1] described the salt $HLiC_2O_4.H_2O$, which was afterwards obtained by Souchay and Lenssen[2] and by Troost.[3] We find but this one salt. The results are given in Table I.:

[1] Ann. Chem. (Liebig), **56**, 221.

[2] *Ibid.*, **100**, 308.

[3] Ann. Chim. Phys., [3], **51**, 103,

Table I.—Solubility of Lithium Oxalate and Oxalic Acid at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Li_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Li_2C_2O_4$ in residue.	Residue contains:
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.66	2.96	68.08	1.10	$H_2C_2O_4.H_2O$ and $HLiC_2O_4.H_2O$
3	10.54	3.11	47.20	33.38	
4	8.08	3.18	*39.21*	*44.77*	$HLiC_2O_4.H_2O$
5	2.60	5.03	*39.22*	*44.59*	
6	2.16	6.54	24.33	66.23	$HLiC_2O_4.H_2O$ and $Li_2C_2O_4$
7	2.12	6.61	2.84	94.68	
8	none	5.87			$Li_2C_2O_4$
Cal. for $HLiC_2O_4.H_2O$			39.46	44.74	

2. *Oxalic Acid and Sodium Oxalate.*

Graham[1] described the compound $HNaC_2O_4.H_2O$, which has been prepared, repeatedly, by others since then. We have found but this one salt. The results are given in Table II. :

Table II.—Solubility of Oxalic Acid and Sodium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Na_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Na_2C_2O_4$ in residue.	Residue contains:
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.48	0.82	68.35	4.35	$H_2C_2O_4.2H_2O$ and $HNaC_2O_4.H_2O$
3	10.52	0.87	63.22	11.18	
4	10.50	0.82	50.26	29.67	
5	9.15	0.71	*35.15*	*52.50*	$HNaC_2O_4.H_2O$
6	6.88	0.86	*34.49*	*51.19*	
7	1.14	1.25	*34.63*	*51.84*	
8	0.47	3.20	*34.50*	*51.66*	
9	0.42	3.84	27.30	62.67	$HNaC_2O_4.H_2O$ and $Na_2C_2O_4$
10	0.43	3.86	3.27	95.79	
11	none	3.60			$Na_2C_2O_4$
Cal. for $HNaC_2O_4.H_2O$			34.60	51.55	

3. *Oxalic Acid and Potassium Oxalate.*

There are two well-known acid potassium oxalates,

$H_3K(C_2O_4)_2.2H_2O$ and HKC_2O_4.

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[1] Ann. Chem. Liebig, 29, 1.

The latter salt, according to Wyrouboff,[1] is anhydrous above 15° and contains water of crystallization below that temperature. There appears to be some doubt as to the amount of water of crystallization present in this salt. Nichols[2] gives the formula $2H_2K_2(C_2O_4)_2.H_2O$, which agrees with Rammelsberg,[3] while Wyrouboff assigns the formula $HKC_2O_4.H_2O$, which agrees with Graham.[4] At 25° we obtained the anhydrous salt. We have also found a third salt, $H_2C_2O_4.2K_2C_2O_4.2H_2O$, which does not appear in the literature. This salt forms only under a narrow range of conditions and does not recrystallize, which probably accounts for its not having been described previously. The results obtained are in Table III. :

Table III.—Solubility of Oxalic Acid and Potassium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $K_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $K_2C_2O_4$ in residue.	Residue contains :
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.30	0.03	68.67	6.34	$H_2C_2O_4.2H_2O$
3	10.30	0.08	58.44	22.68	and
4	10.34	0.02	53.66	32.58	$H_3K(C_2O_4)_2.2H_2O$
5	9.26	0.13	*53.04*	*32.66*	$H_3K(C_2O_4)_2.2H_2O$
6	3.39	0.63	*53.00*	*33.54*	
7	2.05	4.23	51.10	36.13	$H_3K(C_2O_4)_2.2H_2O$
8	2.08	4.27	38.96	59.66	and
9	2.05	4.33	34.94	65.10	HKC_2O_4
10	1.16	11.50	*34.81*	*64.80*	HKC_2O_4
11	0.99	16.93	*34.98*	*65.49*	
12	0.85	21.06	34.89	65.52	HKC_2O_4 and
13	0.86	21.12	22.22	71.37	$H_2K_4(C_2O_4)_3.2H_2O$
14	0.82	21.49	*19.50*	*73.60*	$H_2K_4(C_2O_4)_3.2H_2O$
15	0.64	23.52	*19.65*	*73.58*	
16	0.57	24.88	*19.51*	*73.61*	
17	0.42	27.52	17.56	74.47	$H_2K_4(C_2O_3)_3.2H_2O$
18	0.45	27.52	3.50	86.68	and $K_2C_2O_4.H_2O$
19	none	27.40			$K_2C_2O_4.H_2O$

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[1] Centrabl., **2**, 843 (1900).

[2] Chem. News, **22**, 14.

[3] Pogg. Ann., **93**, 24.

[4] Ann. Chem. (Liebig), **29**, 1.

Below is given the theoretical composition of the three acid salts, with the average results obtained by analysis. Water was found by difference :

	Per cent $H_2C_2O_4$.	Per cent $K_2C_2O_4$.	Per cent H_2O.
$H_3K(C_2O_4)_2.2H_2O$ (theory)	53.12	32.70	14.18
" (found)	53.02	33.10	13.88
HKC_2O_4 (theory)	35.12	64.88	. .
" (found)	34.90	65.15	. .
$H_2K_4(C_2O_4)_3.2H_2O$ (theory)	19.63	72.51	7.86
" (found)	19.55	73.60	6.85

4. *Oxalic Acid and Caesium Oxalate.*

No oxalate of caesium appears to have been described. Caesium oxalate was made by neutralizing caesium carbonate with oxalic acid and evaporating to crystallization. Analysis, by titrating with potassium permanganate, gave :

	Calculated for $Cs_2C_2O_4.H_2O$.	Found.
$Cs_2C_2O_4$	95.16	95.26
H_2O (by diff.)	4.84	4.74

The salt has, therefore, the composition $Cs_2C_2O_4.H_2O$. Its solubility in water, at 25°, is very great, the solution containing 75.82 per cent of anhydrous salt.

The solubility of the mixtures of caesium oxalate and oxalic acid is given in Table IV. :

Table IV.—Solubility of Oxalic Acid and Caesium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Cs_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Cs_2C_2O_4$ in residue.	Residue contains :
1	10.20	none			$H_2C_2O_4.2H_2O$
2	10.29	0.73	67.20	6.90	$H_2C_2O_4.2H_2O$ and $H_3Cs(C_2O_4)_2.2H_2O$
3	10.34	0.46	45.85	40.70	
4	10.26	0.64	42.00	46.07	
5	7.90	9.92	*38.45*	*51.44*	$H_3Cs(C_2O_4)_2.2H_2O$
6	3.93	23.03	*38.18*	*52.07*	
7	4.11	25.12	*38.53*	*51.28*	
8	4.25	27.55	38.01	51.99	$H_3Cs(C_2O_4)_2.2H_2O$ and $H_4Cs_2(C_2O_4)_3$.
9	4.59	27.59	34.59	. .	
10	4.21	27.51	33.81	64.60	

Table IV. (Continued).—Solubility of Oxalic Acid and Caesium Oxalate at 25°.

	Per cent of $H_2C_2O_4$ in solution.	Per cent of $Cs_2C_2O_4$ in solution.	Per cent of $H_2C_2O_4$ in residue.	Per cent of $Cs_2C_2O_4$ in residue.	Residue contains:
11	4.27	28.30	*32.87*	*66.06*	$H_4Cs_2(C_2O_4)_3$
12	4.33	32.26	*32.27*	*68.10*	
13	4.40	35.90	*32.20*	*67.55*	
14	4.83	40.10	27.71	69.99	$H_4Cs_2(C_2O_4)_3$ and $HCsC_2O_4$
15	4.83	39.82	27.91	72.01	
16	4.79	40.37	23.92	78.92	
17	4.45	42.32	*20.50*	*79.92*	$HCsC_2O_4$
18	3.56	42.44	*20.14*	*79.54*	
19	3.62	47.92	*20.36*	*80.84*	
20	3.05	48.80	*19.93*	*80.45*	
21	1.79	60.46	*20.49*	*81.58*	
22	1.04	68.69	*19.02*	*82.17*	
23	0.92	71.48	18.39	80.44	$HCsC_2O_4$ and $H_6Cs_8(C_2O_4)_7$
24	0.92	70.97	16.68	. .	
25	0.87	71.44	16.32	83.08	
26	0.77	73.45	*15.87*	*83.83*	$H_6Cs_8(C_2O_4)_7$
27	0.76	73.84	*16.01*	. .	
28	0.80	74.04	*15.80*	*83.59*	
29	0.75	74.04	*15.88*	. .	
30	0.75	75.26	7.94	87.71	$H_6Cs_8(C_2O_4)_7$ and $Cs_2C_2O_4.H_2O$
31	0.73	75.14	4.32	90.74	
32	0.76	75.22	3.84	89.64	
33	none	75.82			$Cs_2C_2O_4.H_2O$

In the results, the four italicized groups have a nearly constant residue while the solution varies, so that pure double salts are evidently present. It was not easy to obtain the residues in pure condition toward the caesium end, on account of the very great excess of caesium oxalate in the solution, which was also somewhat syrupy.

The average results obtained for the acid salts, together with the calculated values, are as follows :

	$H_2C_2O_4$.	$Cs_2C_2O_4$.	H_2O.
$H_3Cs(C_2O_4)_2.2H_2O$ (calculated)	38.81	50.84	10.35
“ (found)	38.39	51.60	10.00
$H_4Cs_2(C_2O_4)_3$ (calculated)	33.73	66.27	. .
“ (found)	32.45	67.24	. .
$HCsC_2O_4$ (calculated)	20.28	79.72	. .
“ (found)	20.07	80.42	. .
$H_6Cs_8(C_2O_4)_7$ (calculated)	16.03	83.97	. .
“ (found)	15.89	83.71	. .

The last salt is somewhat complicated in composition, but it is believed the formula given is the correct one. If it were the 1 : 2, corresponding to the new potassium salt, it would contain 11.28 per cent of oxalic acid. As it is removed from a solution containing a large excess of caesium oxalate, however, the residue analyzed would tend to have less oxalic acid and more caesium oxalate than is required by the theory instead of the reverse, which would be the case if the salt were the 1 : 2.

Comparison of the Solubilities of the Acid Alkali Oxalates.

For the sake of comparison, the solubility results shown in the previous tables, together with those of Walden on the acid ammonium oxalates, have been recalculated to show the molecules of oxalic acid and of alkali oxalate dissolved by 100 molecules of water. In recalculating, the average solubility results were used where a mixture of two salts was present. These results are given in the following tables, the numbers in the first column referring to the corresponding results in the preceding tables, where the percentage composition of the solutions was given :

Table V.—Oxalic Acid and Lithium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $Li_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.457	0.622
3	“	“
4	1.823	0.633
5	0.563	0.962
6	0.469	1.273
7	“	“
8	none	1.101

Table VI.—Oxalic Acid and Sodium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $Na_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.370	0.130
3	"	"
4	"	"
5	2.032	0.106
6	1.493	0.125
7	0.234	0.172
8	0.098	0.446
9	0.090	0.541
10	"	"
11	none	0.502

Table VII.—Oxalic Acid and Ammonium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $(NH_4)_2C_2O_4$ to 100 molecules H_2O.
1	2.281	0.045
2	"	"
3	"	"
4	1.570	0.072
5	0.546	0.373
6	0.599	0.566
7	0.745	0.791
8	0.781	0.824
9	"	"
10	"	"
11	"	"
12	0.741	0.853
13	0.671	1.00
14	0.645	1.13
15	0.599	1.14
16	"	"
17	"	"
18	"	"
19	"	"
20	none	0.775

Table VIII.—Oxalic Acid and Potassium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $K_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.302	0.005
3	"	"
4	"	"
5	2.046	0.016
6	0.707	0.071
7	0.440	0.495
8	"	"
9	"	"
10	0.266	1.427
11	0.240	2.235
12	0.221	2.928
13	"	"
14	0.211	2.998
15	0.169	3.361
16	0.153	3.617
17	0.122	4.14
18	"	"
19	none	4.09

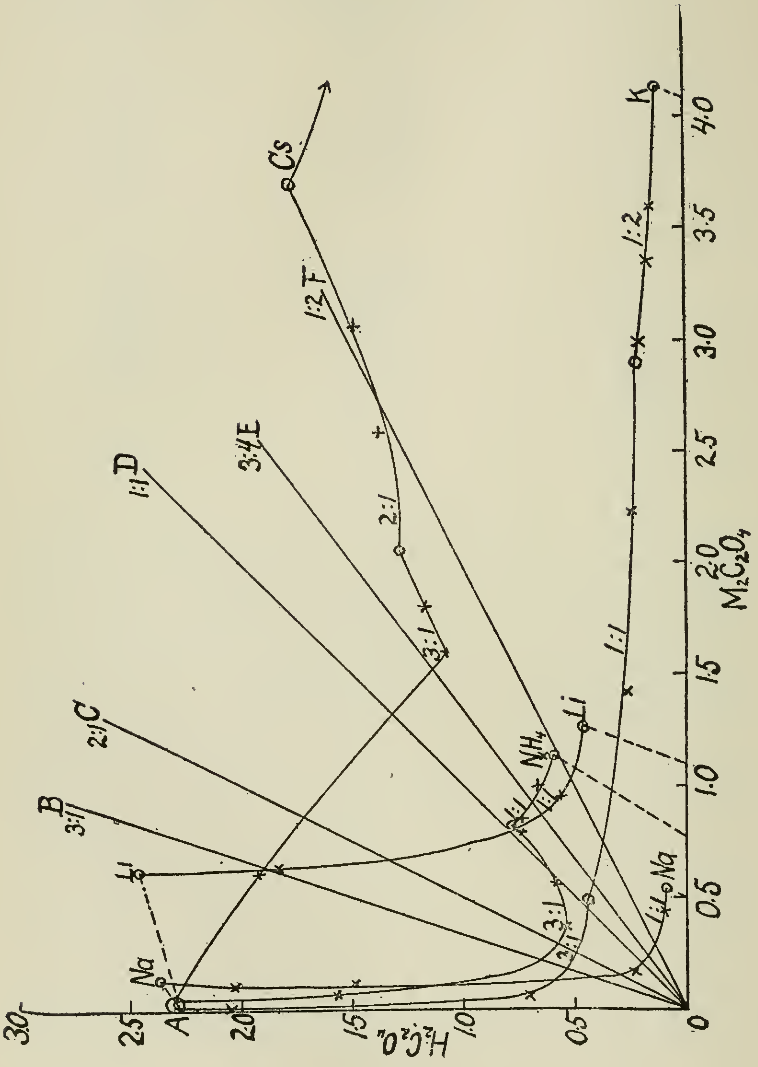
Table IX.—Oxalic Acid and Caesium Oxalate.

	Molecules $H_2C_2O_4$ to 100 molecules H_2O.	Molecules $Cs_2C_2O_4$ to 100 molecules H_2O.
1	2.274	none
2	2.314	0.035
3	"	"
4	"	"
5	1.924	0.614
6	1.077	1.61
7	1.162	1.81
8	1.279	2.06
9	"	"
10	"	"
11	1.267	2.14
12	1.367	2.59
13	1.476	3.07
14	1.752	3.71
15	"	"
16	"	"
17	1.673	4.05

Table IX. (Continued).—Oxalic Acid and Caesium Oxalate.

	Molecules $C_2H_2O_4$ to 100 molecules H_2O.	Molecules $Cs_2C_3O_4$ to 100 molecules H_2O.
18	1.320	4.00
19	1.495	5.04
20	1.268	5.16
21	0.949	8.16
22	0.688	11.56
23	0.648	13.06
24	"	"
25	"	"
26	0.598	14.51
27	0.599	14.81
28	0.636	14.99
29	0.596	14.96
30	0.625	15.93
31	"	"
32	"	"
33	none	15.97

The above results (Tables V.–IX.) are shown in the diagram, where the molecules of oxalic acid are plotted as ordinate and the molecules of alkali oxalate as abscissa. The results for caesium oxalates are not plotted beyond the point corresponding to a mixture of $H_4Cs_2(C_2O_4)_3$, and $HCsC_2O_4$, as they would run beyond the limits of the diagram. A, on the ordinate, represents the solubility of pure oxalic acid and from this point run dotted lines—some of them very short—showing the solubility of oxalic acid in solutions containing small quantities of the alkali oxalates. The solubility of each alkali oxalate alone is represented by a point on the abscissa and the dotted lines show the varying solubility of each oxalate in the presence of small amounts of oxalic acid in solution. The form of these curves was not determined by experiment, so they are represented as straight lines. The dotted lines running from A end in points representing the solubility of oxalic acid with an acid salt, while the dotted lines running from the abscissa end in points showing the solubility of each alkali oxalate in the presence of an acid salt. From the points where the dotted lines end, the curves represent the solubility of a pure


H$_2$C$_2$O$_4$
0
0.5
1.0
1.5
2.0
2.5
3.0
M$_2$C$_2$O$_4$
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
A
3:1 B
2:1 C
1:1 D
3:4 E
1:2 F
Cs
K
Li
NH$_4$
Na
Li
Na
3:1
2:1
1:1
1:2
3:1
3:1
1:1
2:1
1:1
1:1
1:1

acid salt. In the case of lithium and of sodium there is but one curve, as but one acid salt forms. With ammonium, potassium and caesium, which form more than one acid salt, the curves consist of two or more parts, representing the varying solubility of each salt. The points where two salts are present together are represented on the curves by circles and are the points where the different parts of the curve intersect. The salt is indicated which is present along each curve.

In comparing the curves, it will be noted that the oxalates of sodium, lithium and ammonium show very limited solubility and, of these three, ammonium forms one more salt than the other two, which agrees with the general observation that ammonium has more tendency to form double salts than sodium or lithium. On the other hand, comparing the oxalates of ammonium, potassium and caesium, all with a pronounced tendency toward double salt formation, it will be noted that the number of acid salts increases with the solubility of the single oxalates. Judging from the solubility curves, the reason that ammonium oxalate does not form as many acid salts as potassium oxalate is that their formation, toward the ammonium end, is excluded by the limited solubility of ammonium oxalate.

Whether a salt can be recrystallized or not, at 25°, can readily be determined from the diagram.[1] For instance, suppose it is to be determined whether the salt $HLiC_2O_4.H_2O$ can be recrystallized or not. If the salt is dissolved in water it will form a solution containing equal molecules of lithium oxalate and oxalic acid and the composition of the solution will be represented by some point on the line OD. This line cuts the curve of solubility of the salt $HLiC_2O_4.H_2O$, showing that this salt can be in equilibrium with solutions containing an eqnal number of molecules of lithium oxalate and oxalic acid. The salt can, therefore, be recrystallized. On the other hand, the line OD just fails to intersect the curve of solubility for the double salt $HNH_4C_2O_4.\frac{1}{2}H_2O$, but intersects, instead, the curve for the salt $H_3NH_4(C_2O_4)_2.2H_2O$. On recrystallizing, therefore, the 1 : 1 salt would, at first, yield the 3 : 1, followed by a mixture of the 3 : 1 and 1 : 1.

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[1] Van 't Hoff: "Vorles. über Bild. u. Spaltung von Doppelsalzen."

The lines OB, OC, OD, OE and OF represent solutions of the salts $H_3M(C_2O_4)_2$, $H_4M_2(C_2O_4)_3$, HMC_2O_4, $H_6M_8(C_2O_4)_7$ and $H_2M_4(C_2O_4)_3$, respectively, where M represents an alkali metal or ammonium. By noting the intersections of these lines with the curves for the acid salts, the conduct of each salt, on recrystallizing at 25°, can be given.

3 : 1 Salts.—The line OB cuts the curves of solubility of the salts $H_3Cs(C_2O_4)_2.2H_2O$, $H_3NH_4(C_2O_4)_2.2H_2O$ and $H_3K(C_2O_4)_2.2H_2O$. These salts can be recrystallized.

2 : 1 Salts.—Only $H_4Cs_2(C_2O_4)_3$ is known. The line OC, corresponding to solutions of this salt, cuts the curve of solubility of the 3 : 1 salt. On recrystallizing, the 2 : 1 yields the 3 : 1.

1 : 1 Salts.—The line OD cuts the solubility curves of the 1 : 1 salts for lithium and sodium. These salts recrystallize. It cuts the solubility curves of the 3 : 1 salts for caesium, ammonium and potassium. The 1 : 1 salts of these metals, therefore, yield the 3 : 1 salt when first recrystallized. The line comes so near the point of intersection of the curves for the 1 : 1 and 3 : 1 salts for potassium and ammonium, however, that after a small amount of the 3 : 1 salt had formed a mixture of the 3 : 1 and 1 : 1 would separate.

3 : 4 Salts.—Only the caesium salt of this type forms. It yields the 3 : 1 on recrystallizing.

1 : 2 Salts.—Only the potassium salt forms. It yields the 1 : 1 salt on recrystallizing.

SHEFFIELD LABORATORY,
NEW HAVEN, CONN.,
March, 1905.

ON CERTAIN ALLEGED DOUBLE OXALATES.

BY H. W. FOOTE AND I. A. ANDREW.

The following double alkali oxalates are mentioned in the literature :

$KNaC_2O_4$,[1] $NH_4KC_2O_4$,[2] $NH_4LiC_2O_4$.[3]

Although the formation of these double oxalates has been doubted,[1] it seemed worth while to test for them by the solubility method, used in the two preceding articles. Two mixtures were prepared in each case, each containing an excess of one oxalate or the other and the solubility was determined at 25°.

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[1] Wenzel, mentioned by Rammelsberg : Pogg. Ann., **79**, 562.

[2] Wenzel, mentioned by Souchay and Lenssen : Ann. Chem. (Liebig), **99**, 31.

[3] Ladenburg : Handwörterb. der Chemie, 8, 398.

In the mixtures of sodium and potassium oxalates, potassium was determined as potassium platinic chloride and total oxalate by titration with permanganate, from which the amount of each oxalate was calculated. Where ammonium and potassium oxalates or ammonium and lithium oxalates were present, ammonium was determined by distilling from sodium hydroxide into standard acid and total oxalate by titrating with permanganate.

The following results were obtained :

Table I.—Solubility of Sodium and Potassium Oxalates at 25°.

	$K_2C_2O_4$ in solution.	$Na_2C_2O_4$ in solution.	$K_2C_2O_4$ in residue.	$Na_2C_2O_4$ in residue.	Residue contains.
1	27.40	none			$K_2C_2O_4.H_2O$
2	26.22	2.37	83.58	6.94	$K_2C_2O_4.H_2O$ and $Na_2C_2O_4$
3	26.09	2.51	7.60	89.46	
4	none	3.60			$Na_2C_2O_4$

Table II.—Solubility of Ammonium and Potassium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	$K_2C_2O_4$ in solution.	$(NH_4)_2C_2O_4$ in residue.	$K_2C_2O_4$ in residue.	Residue contains :
1	none	27.40			$K_2C_2O_4.H_2O$
2	2.80	25.94	6.14	84.24	$K_2C_2O_4.H_2O$ and $(NH_4)_2C_2O_4.H_2O$
3	2.78	25.98	75.68	13.07	
4	5.07	none			$(NH_4)_2C_2O_4.H_2O$

Table III.—Solubility of Ammonium and Lithium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	$Li_2C_2O_4$ in solution.	$(NH_4)_2C_2O_4$ in residue.	$Li_2C_2O_4$ in residue.	Residue contains :
1	none	5.87	5.71	94.75	$Li_2C_2O_4$
2	4.80	5.75	5.71	94.75	$Li_2C_2O_4$ and $(NH_4)_2C_2O_4.H_2O$
3	4.80	5.76	82.40	5.75	
4	5.07	none			$(NH_4)_2C_2O_4.H_2O$

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[1] Rammelsberg : *Loc. cit.*; Souchay and Lenssen : *Loc. cit.*

In the above results it will be noticed that the solubility of the two mixtures in each table was practically constant, though the residues were so different in composition. This could be true only in case the same salts were present in the residue. Had a double salt formed, the two solubility results would have been different. We therefore conclude that the three double oxalates, mentioned at the beginning of the article, do not exist at 25°.

The results obtained agree with the observations of Rammelsberg and of Souchay and Lenssen, though the method used was different.

A large number of double oxalates of ammonium with magnesium, zinc and cadmium have been described and are tabulated in the following list:

Ammonium magnesium oxalates.

$7(NH_4)_2C_2O_4.MgC_2O_4.8H_2O$,[1]
$6(NH_4)_2C_2O_4.MgC_2O_4.10H_2O$,[2]
$6(NH_4)_2C_2O_4.MgC_2O_4.9H_2O$,[1]
$5(NH_4)_2C_2O_4.MgC_2O_4.8H_2O$,[1]
$13(NH_4)_2C_2O_4.5MgC_2O_4.24H_2O$,[1]
$(NH_4)_2C_2O_4.3MgC_2O_4.2H_2O$.[3]

Ammonium zinc oxalates.

$2(NH_4)_2C_2O_4.ZnC_2O_4.3H_2O$,[2]
$(NH_4)_2C_2O_4.ZnC_2O_4.3H_2O$.[4]

Ammonium cadmium oxalates.

$8(NH_4)_2C_2O_4.CdC_2O_4.11H_2O$,[5]
$6(NH_4)_2C_2O_4.CdC_2O_4.9H_2O$,[5]
$4(NH_4)_2C_2O_4.CdC_2O_4.8H_2O$,[6]
$4(NH_4)_2C_2O_4.CdC_2O_4.7H_2O$.[5]

In view of the number of very improbable salts in the above list, it seemed desirable to test for the formation of these double salts by the solubility method. Varying mixtures of ammonium oxalate with each of the others were treated with water and warmed, then placed in the thermostat and shaken at 25°. Solutions and residues were analyzed. Ammonia was determined, as before, by distilling from sodium hydroxide into standard acid and total oxalate by titration with perman-

[1] Souchay and Lenssen: Ann. Chem. (Liebig), **99**, 31.

[2] Kayser: Pogg. Ann., **60**, 140.

[3] Brandes: Schweig. Jour., **27**, 18. Ref. Watts' Dict., **3**, 649.

[4] Beilstein, 3rd Ed., **1**, 642. This refers to Kayser's salt, but is incorrectly quoted.

[5] Souchay and Lenssen: Ann. Chem. (Liebig), **103**, 308.

[6] Rammelsberg: J, prakt. Chem., **65**, 378.

ganate. The amount of each oxalate could then be calculated. The results obtained are in the following tables :

Table IV.—Solubility of Ammonium and Magnesium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	MgC_2O_4 in solution.	$(NH_4)_2C_2O_4$ in residue.	MgC_2O_4 in residue.	Residue contains :
1	5.59	0.60	2.01	73.92	$(NH_4)_2C_2O_4.H_2O$
2	5.32	0.57	81.70	4.66	and $MgC_2O_4.2H_2O$
3	5.07	none			$(NH_4)_2C_2O_4.H_2O$

Table V.—Solubility of Ammonium and Zinc Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	ZnC_2O_4 in solution.	$(NH_4)_2C_2O_4$ in residue.	ZnC_2O_4 in residue.	Residue contains:
1	6.39	1.64	1.19	80.33	$(NH_4)_2C_2O_4.H_2O$ and $ZnC_2O_4.2H_2O$
2	6.11	1.51	39.72	43.91	
3	6.17	1.69	61.78	23.53	
4	6.11	1.58	83.92	3.27	
5	5.07	none			$(NH_4)_2C_2O_4.H_2O$

Table VI.—Solubility of Ammonium and Cadmium Oxalates at 25°.

	$(NH_4)_2C_2O_4$ in solution.	CdC_2O_4 in solution.	$(NH_4)C_2O_4$ in residue.	CdC_2O_4 in residue.	Residue contains:
1	5.08	0.29	8.71	71.33	$(NH_4)_2.C_2O_4.H_2O$ and
2	5.05	0.27	77.06	10.69	$CdC_2O_4.3H_2O$
3	5.07	none			$(NH_4)_2C_2O_4.H_2O$

In each of the above tables it will be noticed that the composition of the solution remains constant, though the residues vary between extreme limits, showing that no double salt has formed. On account of the very slight solubility of magnesium, zinc and cadmium oxalates, in the presence of the saturated solution of ammonium oxalate, it is, further, very probable that no double salts of these oxalates exist at any temperature.

SHEFFIELD CHEMICAL LABORATORY,
NEW HAVEN, CONN.,
March, 1905.

REVIEWS.

TECHNO-CHEMICAL ANALYSIS. By G. LUNGE, Professor at the Eidgenössische Polytechnische Schule at Zurich. Authorized translation by A. I. COHN. New York: John Wiley & Sons. First edition. 1905. pp. 136. Price, $1.00.

The scope of this little book is explained as comprising the examination of raw material for chemical factories and other technical industries, the operative control of chemical factories by chemical and physical means and the examination of the end-products, with respect to the properties which have an important bearing on their employment. In many cases empirical methods are used, very often, however, the methods employed in scientific chemical analysis must be adopted, with every attention to extreme accuracy.

The subjects treated are gas analysis, fuels, acids, soda, carbonated lyes, chlorine industry, potassium salts, clay and cement industry, artificial manures, gas and ammonia manufacture, calcium carbide, coal tar industry, mineral oils, oils and fats, soaps, glycerine, sugar, alcohol manufacture, vinegar, wine, beer, tanning and dyeing.

While excellently well adapted to the use of technical chemists, Professor Lunge's book seems rather brief and condensed, but, doubtless, is what is wanted for general use. When employed in connection with the author's larger work, "Chemisch-Technische Untersuchungsmethoden," to which frequent reference is made, it would fill every requirement. E. R.

A SCHEME FOR THE DETECTION OF THE MORE COMMON CLASSES OF CARBON COMPOUNDS. By FRANK E. WESTON, B.SC., F.C.S. London: Longmans, Green & Co. 1904. pp. 56. Price, 2 shillings.

The contents of this book embody the results of seven years' experience and it has been prepared for the use of students intending to submit themselves to two English examining boards. After various preliminary observations, the student is directed to ascertain what elements are present in the compound he is working with, the result he obtains will place it in one of 10 large groups, which are subdivided into 42 smaller ones. As an example, compounds containing carbon, hydrogen and nitrogen are divided into "amines, diamines, hydrazines, alkaloids, pyridine and quinoline and pyrrol and alkyl." This is, presumably, a misprint. The idea of giving students of organic chemistry some work of a qualitative analytical nature is good and has suggested itself to others, as is shown by the preparation of Mulliken's book[1] on the subject, but the present little volume is hardly likely to encourage instruction in this direction. The tests are very often vague, meaningless and, not infrequently, incorrect, as the following examples show: "Deep red coloration (with concentrated sulphuric acid) indicates certain glucosides," p. 5. "To detect *triple* bond, carefully mix substance with ammoniacal Cu_2Cl_2 solution; when colored, insoluble body will be produced," p. 9. "All hydroxy acids when acted on with acid chloride (*sic*) yield esters in which acid residue enters the alcohol—OH group," p. 17. "Only those hydrazones containing an OH group in the α-position to the hydrazine radicle are capable of forming osazones," p. 39. The apparatus illustrated is very antique and inconvenient, except where it is utterly trivial. There is no index. The book must be described as an unhappy attempt to help a rather useful cause. J. B. T.

THEORETICAL CHEMISTRY FROM THE STANDPOINT OF AVOGADRO'S RULE AND THERMODYNAMICS. By PROF. WALTHER NERNST, PH.D., of the University of Göttingen. Revised in accordance with the fourth German edition. By R. A. LEHFELDT, D.SC. London and New York: Macmillan & Co., Limited. 1904. pp. 771. Price, $3.75.

The appearance of the first edition of this important work has already been noticed.[2] The book has now been carefully revised and brought up to date, it is, of course, not adapted to the beginner, but is indispensable to every advanced student of physical chemistry, as well as to every teacher of the subject.

It is a matter for deep regret that we cannot get a satisfactory translation into English of such a book. The present translator states in his preface that "I have translated all the new matter contained in the fourth German edition and revised certain parts of the old, in the endeavor to free the book from any mistakes and ambiguities that a first edition is so liable to contain. The bulk of the old text, however, remains as it was."

The defective nature of the original translation is well known. If we examine the new one we find many of the old defects still remaining, as we should expect from the above admission on the part of the present translator. Indeed, we can scarcely turn to a page where we do not find some violation of good, idiomatic English. In some cases this violation is so glaring as either to obscure the meaning or to leave it ambiguous. The number of examples is so large that it would require an extended review to point them out.

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[1] THIS JOURNAL, 32, 404.
[2] *Ibid.*, 17, 541.

For these reasons the student and teacher are advised to purchase the book in the original German. H. C. J.

THE VARNISHES OF THE ITALIAN VIOLIN-MAKERS OF THE XVI. AND XVII. CENTURIES. By GEORGE FRY, F.L.S., F.C.S. London: Stevens & Sons, Limited. 1904. pp. xii + 170. Price, $1.50.

It appears that Mr. Fry, who is a chemist of long experience, is also a musician. In 1901 his attention became fixed on the varnishes used by the famous old violin-makers to such a degree that he undertook to find out how they were prepared. These varnishes are very elastic and not very hard; hence they cannot be alcoholic spirit varnishes; the general opinion is that they are either oleoresinous or turpentine-spirit varnishes. The author, it seems, knew nothing about the practical part of making or using varnish in general, but he invented, first, a theory that the violin-makers used such products as were naturally found in their own vicinities, namely, colophony, turpentine, turpentine-spirit and linseed oil; and second, varnishes made of these materials resembling those on the old instruments. These old varnishes are from red to brown in color; modern practice is to obtain these tints by dissolving coloring-matter in the otherwise pale-yellow varnish. The author, in brief, dissolves his resinous matter in turpentine spirit and to this adds strong nitric acid, heats the mixture until the color is developed, then adds linseed oil and more turpentine-spirit, if necessary. In general, he uses half as much oil as colophony. These varnishes he declares to be durable, but as his experiments extended over only 2 or 3 years and as it is evident that he was not much accustomed to testing varnishes, this should be regarded as being, as yet, unproved. The book is interesting and valuable; it brings together a large amount of information regarding violin varnishes, while the products invented by the author are, at least, novel. The present reviewer (a varnish-maker) does not believe such varnishes are valuable, but as he has not tried them this is only an opinion; certainly there is no proof that they were known in the past, while there is a large body of evidence to show that amber or other similar varnishes were used for the purpose. Nitric acid, while it has not been employed in this way, has been tried in varnish-making before, but was found to be of no use; no colophony varnish of permanent value has yet been made, although such varnishes are of great antiquity. The trouble with the violin-varnish problem is that it is of no commercial importance; the expert varnish-makers devote their ingenuity and knowledge to make their products as nearly colorless as possible. Beautiful deep-red and brown varnishes may be made of amber and we know that they were made in Italy at the time in question, also at least one learned contemporary stated that they were used on lutes and other musical instruments.

The book is clearly and simply written; it is frankly the *ex parte* argument of a man who is convinced that he is right; the experiments are given in sufficient detail; it contains a bibliography of the subject; it has a very full table of contents, but no index. Many singular and almost uniformly erroneous beliefs about oleoresinous varnishes are stated as facts, but the author is evidently honest and straightforward and a careful and ingenious experimenter. A. H. SABIN.

PRACTICAL EXERCISES IN CHEMICAL PHYSIOLOGY AND HISTOLOGY. Arranged by H. B. LACEY, Head of the Biological Department of the South-Western Polytechnic, Chelsea, and C. A. PANNETT, B.SC, London, Lecturer in Physiology at the South-Western Polytechnic, Chelsea. Cambridge: W. Heffer & Sons; London: Simpkin, Marshall & Co. 1904. pp. 112. Price, 2 shillings, net.

This little manual was devised for English students who are to present themselves for certain examinations. The first 56 pages are devoted to chemical experiments and the latter part to histology. The directions are very explicit and evidently were intended for students who have had no training whatever and merely desire to get quickly some idea of the subject and to pass a good examination in it. A. S. L.

EXERCISES IN PRACTICAL PHYSIOLOGICAL CHEMISTRY. By SYDNEY W. COLE, M.A., Additional Demonstrator in Physiology, Cambridge University. Cambridge: W. Heffer & Sons; London: Simpkin, Marshall & Co. 1904. pp. 152 Price, 5 shillings, net.

This manual is very clearly written and the experiments well described. It contains no special features except a new color test for lactic acid, by F. C. Fopkins, which will probably prove useful.

The book is presented in nice, readable form and commends itself for a brief laboratory course. A. S. L.

CHEMICAL STATICS AND DYNAMICS, Including the Theories of Chemical Change, Catalysis and Explosions. By J. W. MELLOR, D.SC. B.SC., Author of Higher Mathematics for Students of Chemistry and Physics. London, New York and Bombay: Longmans, Green & Co. 1904. pp. 528. Price, $2.00.

The author of this book is well known in connection with the manual referred to above. The same valuable characteristics that appear in the "Higher Mathematics for Students of Chemistry and Physics," manifest themselves in the present work. The material is well selected and treated in a clear and concise manner. The work comprises 14 chapters : Introduction ; Homogeneous Chemical Reactions ; Homogeneous Side Reactions ; Homogeneous Opposing Reactions ; Homogeneous Consecutive Reactions ; The Beginning of a Chemical Reaction ; Heterogeneous Reactions ; Equilibrium and Dissociation ; Electrolytic Dissociation ; Catalysis and the Theory of Chemical Change ; Fermentation ; The Influence of Temperature on Chemical Reactions ; The Influence of Pressure on Chemical Reactions ; Explosions.

Not the least valuable portion of this book is the large number of references to the literature given at the bottom of the pages. It would be a step forward if this principle were adopted in all text-books of an advanced character, at least in physical chemistry.

The book, as a whole, is of the same high character as Findlay's Phase Rule, in this same series. The series, edited by Sir William Ramsay, will doubtless prove to be a valuable addition to physical chemical literature. It is, however, to be regretted that one of the most interesting and important sections of the science—electrochemistry—should have been treated so much less satisfactorily than the remainder. H. C. J.

ELEMENTS OF MINERALOGY, CRYSTALLOGRAPHY AND BLOWPIPE ANALYSIS FROM A PRACTICAL STANDPOINT. By ALFRED J. MOSES, E.M., PH.D., and CHARLES LATHROP PARSONS, B.S. Third enlarged edition. New York : Van Nostrand Co. 1904. Price, $2.50 net.

Earlier editions of this well-known text-book have been reviewed in THIS JOURNAL as they appeared.[1] The present edition follows, in general, the design of the previous issues, but has been considerably enlarged; the chapter on Crystallography has been entirely rewritten and the chapter on Descriptive Mineralogy has been carefully revised and, in parts, rewritten. The text has also been more fully illustrated by the addition of 30 or 40 half-tones, which assist in bringing out the characteristic clustering of different minerals. The substitution of minerals for models in the crystallographic portion is likely to add to the interest of the student and to make him more familiar with a few typical minerals of strong crystallizing power. There are numerous minor criticisms suggested by a perusal of the book, but it will doubtless continue to prove its usefulness in the field to which it is devoted—the discussion and determination of minerals from a practical standpoint.

E. B. M.

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[1] THIS JOURNAL, **17**, 629 (1895) ; **25**, 250 (1901).

THE RECENT DEVELOPMENT OF PHYSICAL SCIENCE. By WILLIAM CECIL DAMPIER WHETHAM, M.A., F.R.S., Fellow of Trinity College, Cambridge. Philadelphia: P. Blakiston's Son & Co. 1904. Price, $2.00 net.

This interesting book might fairly be said to be the work of the Whetham family, since Dr. Whetham states, in his preface, that he "wishes especially to thank his wife for continual correction both of the manuscript and of the proof-sheets and his sister for help with the index." The aim of the work can be shown by a quotation from the preface. "It happens that an acquaintance with the knowledge newly acquired in one department of science is necessary for the study of another; indeed the phenomena which need for their interpretation the methods of two branches of science have proved often the most fruitful field of inquiry. For reasons such as these it has been thought possible that a short account of some of the important investigations now being carried on in the physical laboratories of the world, might prove useful to students of science in general; while it is hoped that, by treating the subjects as far as possible without technical language, the book may also appeal to those, who with little definite scientific training, are interested in the more important conclusions of scientific thought."

The reviewer agrees absolutely with the author in both of these matters. Any one who has had to do with the training of young men in science has been painfully impressed with the narrowness of their knowledge. This may be necessary at first, but if not overcome, later, by the individual, is fatal to his success. Bunsen said, in his day, that "a chemist who is not a physicist is nothing," and this holds much more rigidly today than in the time of Bunsen.

In reference to bringing the main results of scientific investigation to the level of the intelligent public, much might be said. In the opinion of the reviewer men of science, in this respect, often neglect a pressing duty. The chief aim of scientific investigation is the discovery of generalizations, but why do we wish to discuss these so-called Laws of Nature? It is for the good of mankind—not the material, but the intellectual good. That the greatest good should be achieved by scientific investigation, the results should be accessible to the greatest number. This can be accomplished only by books such as the one under discussion.

It is to be regretted that men of science sometimes look upon such work as not quite up to their standard. In taking such a view they greatly limit the sphere of their usefulness to the race. It is a fair question to ask whether the college student always represents the best intellect and whether there are not as strong intellects outside as inside the university? Tyndal did much work of the semi-popular kind, both in his lectures and his books and it is to be hoped that work of this character will be greatly increased in the future. In this way only can that large number of highly intelligent people, who, for one reason or another have been barred from a university career, be shown the true grandeur of scientific investigation.

The reviewer must take exception to what Dr. Whetham says on page 30 and following, in reference to "Laws of Nature." The discovery of generalization or "Law" is the highest aim of the investigator. Beyond this, at present, he cannot go. Whether these generalizations, in any case, correspond to ultimate truths we do not know and have no means, at present, of finding out. It is, therefore, much more nearly correct to say that the highest aim of the scientific investigator is the discovery of generalization, than to say that it is the discovery of truth.

The book discusses; The Philosophical Basis of Physical Science; The Liquefaction of Gases and the Absolute Zero of Temperature; Fusion and Solidification; The Problems of Solution; The Conduction of Electricity through Gases; Radio-Activity, Atoms and Ether; Astro-Physics.

H. C. J.

VOL. XXXIV. SEPTEMBER, 1905. NO. 3.

AMERICAN

CHEMICAL JOURNAL

Contributions from the Sheffield Laboratory of Yale University.

CXXV.—RESEARCHES ON PYRIMIDINES: THE ACTION OF AQUEOUS AND ALCOHOLIC AMMONIA AND ANILINE ON SOME HALOGEN AND MERCAPTO PYRIMIDINES.

[TENTH PAPER.]

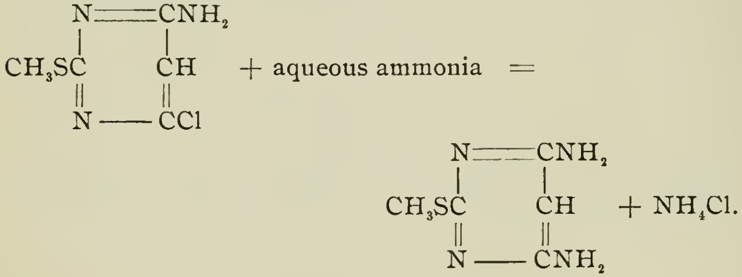
BY TREAT B. JOHNSON AND CARL O. JOHNS.

The object of this paper is to describe the behavior of certain halogen and mercapto pyrimidines towards ammoniacal solutions and aniline.

We have had occasion, in the preparation of aminopyrimidines, to use both aqueous and alcoholic solutions of ammonia to replace, with the amino group, halogens and mercapto radicals in pyrimidines. We have been greatly impressed, in the course of this work, with the remarkable difference in degree of reactivity of aqueous and alcoholic ammonia towards such pyrimidine derivatives.

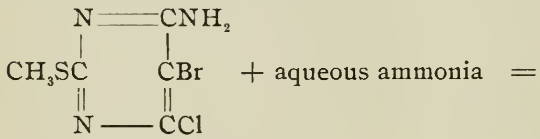
In a recent publication from this laboratory, by Wheeler and

Jamieson,[1] it was shown that when 2-methylmercapto-5-methyl-4,6-dichlorpyrimidine was heated with alcoholic methylamine, only 1 chlorine atom was removed and 2-methylmercapto-4-chlor-5-methyl-6-methylamino pyrimidine was the product of the reaction. An analogous result was obtained when 2-methylmercapto-4,6-dichlorpyrimidine was heated with alcoholic ammonia. It was converted, practically quantitatively, into 2-methylmercapto-4-chlor-6-aminopyrimidine. They did not succeed in converting this chloraminopyrimidine into the corresponding diaminopyrimidine (I.) by heating with alcoholic ammonia. We now find that the 2-methylmercapto-4-chlor-6-aminopyrimidine is converted, quantitatively, into 2-methylmercapto-4,6-diaminopyrimidine (I.) when heated with aqueous ammonia, at 185°–195°:



I.

It seemed of interest, in connection with this result, to compare the behavior of aqueous and alcoholic ammonia towards 2-methylmercapto-4-chlor-5-brom-6-aminopyrimidine. This compound reacts in an analogous manner to the above 2-methylmercapto-4-chlor-6-aminopyrimidine. It can be recovered unaltered after heating with concentrated alcoholic ammonia, at 150°–160°. When heated with aqueous ammonia, under the same conditions, (150°–160°), it was converted, quantitatively, into 2-methylmercapto-5-brom-4,6-diaminopyrimidine,



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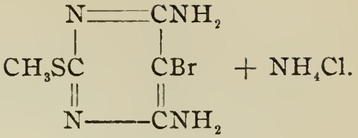
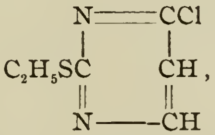
[1] This Journal, 32, 343 (1904).

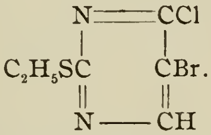


II.

It would appear, from the results of these two experiments, that a halogen is more easily replaced by the amino group when aqueous ammonia is used. In order to test this assumption further and to compare the action of ammoniacal solutions in another series, we have examined the comparative behavior of 2-ethylmercapto-6-chlorpyrimidine (III.) and 2-ethylmercapto-5-brom-6-chlorpyrimidine[1] (IV.) towards aqueous and alcoholic ammonia:



III.



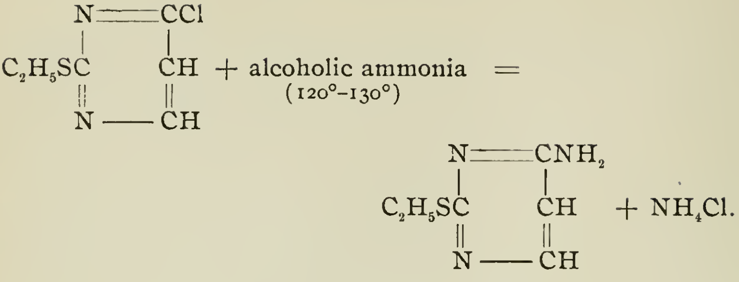
IV.

Wheeler and Johnson[2] observed that 2-ethylmercapto-6-chlorpyrimidine reacts with alcoholic ammonia, at 140°–150°, to form 2-ethylmercapto-6-aminopyrimidine[3] (V.). We now find that this same chlorpyrimidine can be heated with aqueous ammonia, at the same temperature, (140°–150°) and be recovered unaltered. A most remarkable case of lack of analogy was observed when we examined the behavior of ammoniacal solutions towards 2-ethylmercapto-5-brom-6-chlorpyrimidine (IV.). This pyrimidine was converted, quantitatively, into 2-ethylmercapto-5-brom-6-aminopyrimidine (VI.) when heated with alcoholic ammonia, at 120°–130° and also when heated with aqueous ammonia, at 140°–150°.

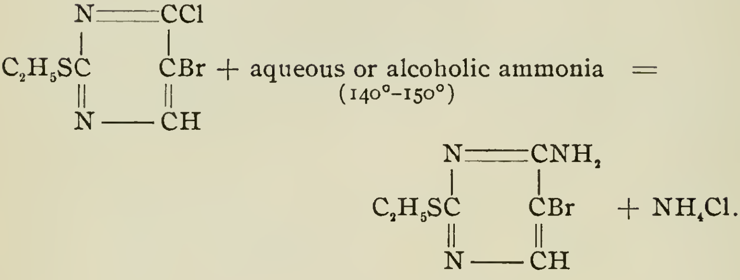
[1] Wheeler and Johnson: THIS JOURNAL, **31**, 603 (1904).

[2] *Ibid.*, **29**, 492 (1903).

[3] It has been our experience, since the publication of this paper, that the best yield of this 2-ethylmercapto-6-aminopyrimidine is obtained when the chloride is heated with alcoholic ammonia, at 120°–130°, for 3 or 4 hours. T. B. J.

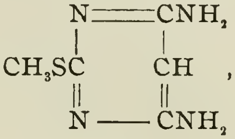


V.

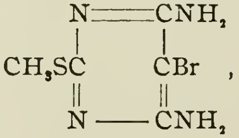


VI.

The abnormal behavior of ammoniacal solutions was also illustrated when we tried to replace the mercapto radical, in certain pyrimidines, with the amino group. 2-Methylmercapto-4,6-diaminopyrimidine[1] (VII.) and 2-methylmercapto-5-brom-4,6-diaminopyrimidine (VIII.) were recovered unaltered, after heating with both aqueous and alcoholic ammonia, at 205°–215°. These two negative results were of especial interest



VII.



VIII.

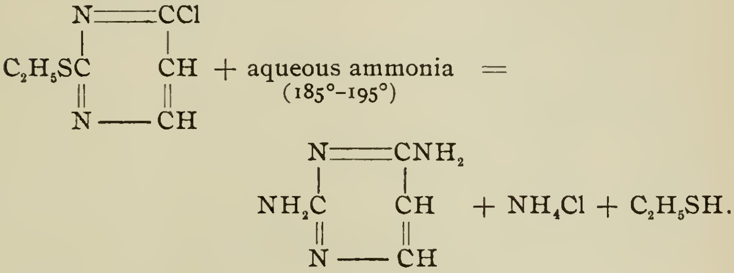
when compared with the behavior of 2-ethylmercapto-6-chlorpyrimidine[2] and 2-ethylmercapto-5-brom-6-chlorpyrimidine[3] towards aqueous ammonia, at high temperatures. When

[1] Wheeler and Jamieson : *Loc. cit.*

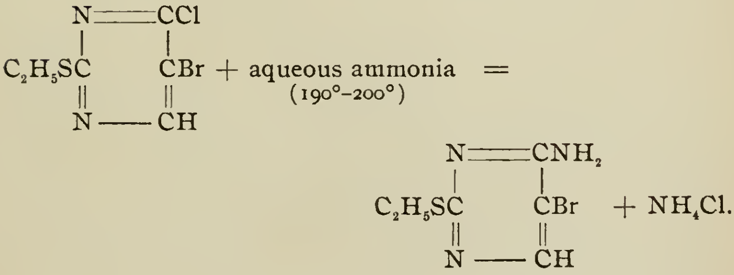
[2] Wheeler and Johnson : This Journal, **29**, 496 (1903).

[3] Wheeler and Johnson : *Ibid.*, **31**, 603 (1904).

2-ethylmercapto-6-chlorpyrimidine was heated with aqueous ammonia, at 185°–195°, 2,6-diaminopyrimidine[1] (IX) was the product of the reaction. On the other hand, when 2-ethylmercapto-5-brom-6-chlorpyrimidine was heated, under practically the same conditions, (190°–200°) with aqueous ammonia, the chlorine atom only was removed and 2-ethylmercapto-5-brom-6-aminopyrimidine (X.) was formed:



IX.



X.

It has been our experience that a mercapto group is more easily replaced by the anilido—NHC_6H_5—than by the amino group. When 2-methylmercapto-4-chlor-6-aminopyrimidine was heated with 1 molecular proportion of aniline, at 120°–130°, 2-methylmercapto-4-anilido-6-aminopyrimidine (XI.) was formed. On the other hand, when heated with 2 molecular proportions of aniline, at 140°–150°, 2,4-dianilido-6-aminopyrimidine (XII.) was the product of the reaction.

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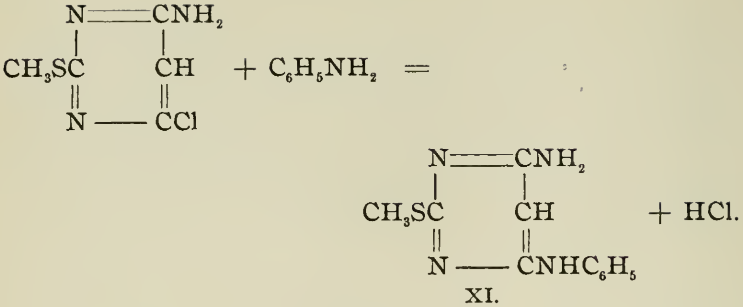
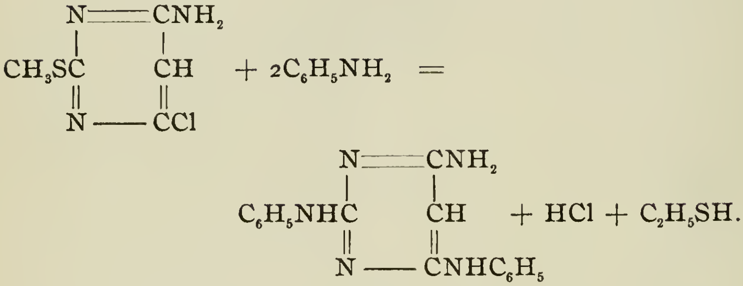
[1] Büttner: Ber. d. chem. Ges., **36**, 2233.

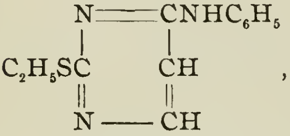


XI.

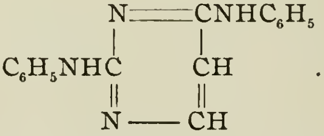


XII.

These results are analogous to that obtained by Wheeler and Bristol.[1] They observed that 2-ethylmercapto-6-chlorpyrimidine reacted with 1 molecular proportion of aniline, at 100°, to form 2-ethylmercapto-6-anilidopyrimidine (XIII.). When the same mercaptochlorpyrimidine was heated with 2 molecular proportions of aniline, at 150°, it was converted into 2,6-dianilidopyrimidine (XIV.):



XIII.



XIV.

2-Methylmercapto-4-anilido-6-aminopyrimidine (XI.) reacts with bromine, in glacial acetic acid, to form a dibrom substitution-product, melting at 202°. In order to establish the structure of this body it was necessary to decide whether 1 or 2 bromine atoms had entered the benzene nucleus; whether 2-methylmercapto-4-dibromanilido-6-aminopyrimidine (XV.) or 2-methylmercapto-4-parabromanilido-5-brom-6-aminopyrimidine (XVI.) was the product of the reaction. The following experiment proved that formula XVI. represents the structure

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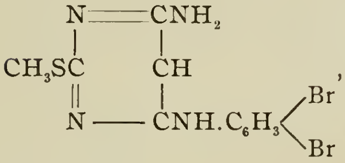
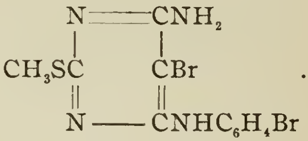
[1] This Journal, **33**, 448 (1905).

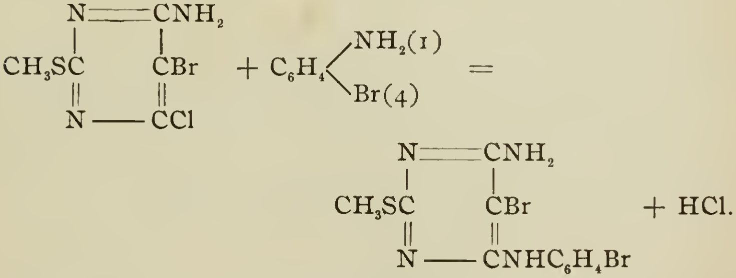


XV.



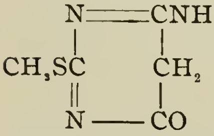
XVI.

of this dibrompyrimidine. The same derivative, melting at 202°, was obtained when 2-methylmercapto-4-chlor-5-brom-6-aminopyrimidine was heated with parabromaniline:



EXPERIMENTAL.

2-Methylmercapto-4-oxy-6-aminopyrimidine,



.—This mercaptopyrimidine was easily prepared by dissolving 2-thio-4-oxy-6-aminopyrimidine[1] in alcohol, containing 1 molecular proportion of sodium ethylate and then warming on the steam-bath with 1 molecular proportion of methyl iodide. The reaction is exceedingly smooth and in a few minutes the mercapto derivative separates from the alcoholic solution. The pyrimidine was purified by evaporating the excess of alcohol and then washing the crystalline residue with cold water, to remove sodium iodide. It was difficultly soluble in hot alcohol, from which it separated in colorless plates. It decomposed at 267° with effervescence. The yield was practically quantitative. Analysis :

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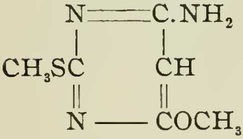
[1] The 2-thio-4-oxy-6-aminopyrimidine used for this preparation was made according to Traube's directions, by condensing thiourea with cyanethylacetate, in presence of sodium ethylate. Ann. Chem. (Liebig), **331**, 71.

	Calculated for $C_5H_7ON_3S$.	Found.
N	26.75	26.97

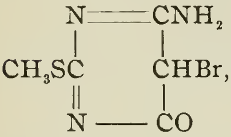
2-Methylmercapto-4-methoxy-6-aminopyrimidine,



.—This compound was obtained when 2-thio-4-oxy-6-aminopyrimidine was warmed, in alcohol, with 2 molecular proportions of sodium ethylate and methyl iodide. It was soluble in acids but insoluble in alkali. It was purified by crystallizing from alcohol, from which it separated, on cooling, in long, well-developed prisms. It melted at 256°, without effervescence, to a clear oil. Analysis (Kjeldahl) :

	Calculated for $C_6H_9ON_3S$.	Found.
N	24.55	24.46

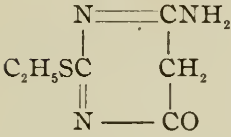
2-Methylmercapto-4-oxy-5-brom-6-aminopyrimidine,



, was prepared by dissolving 2-methylmercapto-4-oxy-6-aminopyrimidine in glacial acetic acid and then adding the calculated quantity of bromine. The bromine color disappeared at once and the pyrimidine separated as a beautiful, crystalline powder. It was difficultly soluble in water and alcohol. It crystallized from hot acetic acid in slender prisms. It had no definite melting-point, but began to turn brown at 200° and did not melt below 300°. Analysis (Kjeldahl):

	Calculated for $C_5H_6ON_3SBr$.	Found.
N	17.79	17.76

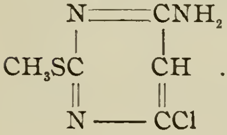
2-Ethylmercapto-4-oxy-6-aminopyrimidine,



.—This compound was prepared in a manner similar to that used for the preparation of 2-methylmercapto-4-oxy-6-aminopyrimidine, by warming 2-thio-4-oxy-6-aminopyrimidine, in alcohol, with molecular proportions of sodium ethylate and ethyl bromide. It was very soluble in alcohol. It crystallized from water in long, slender prisms and melted at 216°–217°, to a clear oil. Analysis (Kjeldahl):

	Calculated for $C_6H_9ON_3S$.	Found.
N	24.56	24.37

2-Methylmercapto-4-chlor-6-aminopyrimidine,



.—This derivative was previously described by Wheeler and Jamieson,[1] who obtained it by heating 2-methylmercapto-4,6-dichlorpyrimidine with alcoholic ammonia. We find that it can be prepared more easily by treating 2-methylmercapto-4-oxy-6-aminopyrimidine with phosphorus oxychloride. The pyrimidine was boiled with an excess of phosphorus oxychloride until the evolution of hydrochloric acid ceased. The clear solution which resulted was then heated to 100°, under diminished pressure, to remove the excess of phosphorus oxychloride. A brittle, amorphous residue was obtained. This proved to be a mixture of the hydrochloride of the unaltered pyrimidine and an unstable phosphorus derivative of the mercaptochlorpyrimidine. The amorphous residue was carefully decomposed with ice-water. We obtained a clear, yellow solution, which was then made distinctly alkaline with ammonium hydroxide and concentrated by evaporation on the steam-bath. Upon cooling, a crystalline product separated which proved to be a mixture of the 2-methylmercapto-4-chlor-6-aminopyrimidine and unaltered 2-methylmercapto-4-oxy-6-aminopyrimidine. A separation of the two compounds was effected by washing with dilute sodium hydroxide solution, in which the chlorpyrimidine is insoluble. It was further purified by recrystallizing from water. It agreed in all its properties with the compound described by Wheeler and Jamieson,[1] except that we found it to melt at 132° instead of 126°–127°. Analysis (Kjeldahl):

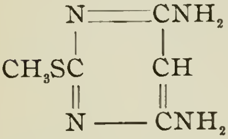
---

[1] This Journal, **32**, 343 (1904).

	Calculated for $C_5H_6N_3SCl$.	Found.
N	23.93	23.86

In our experiments in the preparation of the above 2-methylmercapto-4-chlor-6-aminopyrimidine we have usually obtained only about 45–50 per cent of the theoretical yield. In one experiment the yield corresponded to 59.6 per cent of the theoretical. In nearly every case we recovered, unaltered, about one-half of the 2-methylmercapto-4-oxy-6-aminopyrimidine. Phosphorus pentachloride was used in one experiment in place of phosphorus oxychloride, but the reaction was not as smooth and more decomposition-products were formed.

2-Methylmercapto-4,6-diaminopyrimidine,



.—This compound has been described in a previous paper from this laboratory.[2] We prepared it by heating the above 2-methylmercapto-4-chlor-6-aminopyrimidine with concentrated aqueous ammonia, at 185°–195°, for 5 hours. When the tube was opened we obtained a colorless solution which was immediately concentrated on the steam-bath. Upon cooling, a beautiful, crystalline body separated, which was purified by recrystallizing from water and alcohol. It deposited in lenticular-shaped crystals and melted at 184°–185°, to a clear oil. Analysis (Kjeldahl):

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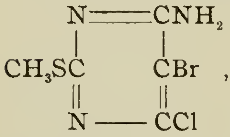
[1] *Loc. cit.*

[2] Wheeler and Jamieson: *Loc. cit.*

	Calculated for $C_5H_8N_4S$.	Found.
N	35.89	35.54

This mercaptodiaminopyrimidine is very stable in the presence of aqueous and alcoholic ammonia solutions. It was recovered, unaltered, after heating with concentrated aqueous ammonia, for 7 hours, at 205°–215°. It was then heated with a saturated, alcoholic solution of ammonia, for 7 hours, at 205°–215°. The pyrimidine was again recovered unaltered and melted sharply at 184°–185°.

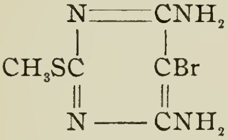
2-Methylmercapto-4-chlor-5-brom-6-aminopyrimidine, , was obtained in the form of its hydrobromic acid salt, when a molecular proportion of bromine was added to an acetic acid solution of 2-methylmercapto-4-chlor-6-aminopyrimidine. The hydrobromide sintered at about 180°–190° and then decomposed at 208°, with violent effervescence. It was purified for analysis by crystallizing from acetic acid, from which it separated, on cooling, in stout prisms. Analysis:

	Calculated for $C_5H_6N_3SClBr_2$.	Found.
N	12.51	12.56

The pyrimidine base was easily obtained from its salt by treating with a 10 per cent solution of sodium hydroxide. It was difficultly soluble in water and melted at 165°, without effervescence. The pyrimidine showed a strong tendency to occlude water. In order to thoroughly dry it for analysis it was necessary to heat for about 1 hour, at 115°–120°. Analysis:

	Calculated for $C_5H_5N_3SClBr$.	Found.
N	16.50	16.38

2-Methylmercapto-5-brom-4,6-diaminopyrimidine,

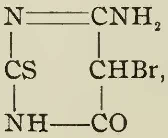


.—This derivative was prepared by heating 2-methylmercapto–4–chlor–5–brom–6–aminopyrimidine with aqueous ammonia, for 4 hours, at 150°–160°. When the tube was opened the compound had separated in magnificent prisms. Some of these crystals measured 3 cm. in length. The pyrimidine crystallized from hot water in beautiful prisms and melted at 192°, to a clear oil. The yield corresponded to about 80 per cent of the theoretical. Analysis (Kjeldahl):

	Calculated for $C_5H_7N_4SBr$.	Found.
N	23.83	23.77

An attempt was made to prepare this diaminopyrimidine by heating the 2-methylmercapto-4-chlor-5-brom-6-aminopyrimidine with alcoholic ammonia. After heating for 4 hours, at 150°–160°, it was recovered unaltered. The alcohol solution gave only a faint test for chlorine. The 2-methylmercapto-5-brom-4,6-diaminopyrimidine is very stable in contact with aqueous and alcoholic ammonia, at higher temperatures. After heating for 8 hours, at 180°–190°, with concentrated, aqueous ammonia, it was recovered unaltered. It was again heated with fresh aqueous ammonia, for 5 hours, at 200°–210°. Only a trace of mercaptan could be detected and the pyrimidine was recovered, melting sharply at 192°. A similar result was obtained when it was heated with concentrated, alcoholic ammonia, for 4 hours, at 200°–214°.

2-Thio-4-oxy-5-brom-6-aminopyrimidine,

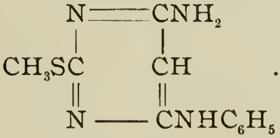


, was

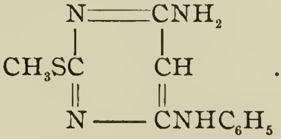
made by adding a molecular proportion of bromine to an acetic acid solution of 2-thio-4-oxy-6-aminopyrimidine. It separated from the acetic acid in granular crystals. It was difficultly soluble in acetic acid and insoluble in water. It did not melt below 300°. Analysis (Kjeldahl) :

	Calculated for $C_4H_4ON_3SBr$.	Found.
N	18.91	18.68

2-Methylmercapto-4-anilido-6-aminopyrimidine,



.—Four grams of 2-methylmercapto-4-chlor-6-aminopyrimidine were heated with 1 molecular proportion of aniline, for 6 hours, at 100°–130°. A clear, red varnish was obtained, which dissolved in boiling alcohol. Upon cooling, rhombic-shaped prisms separated. They were purified by recrystallizing from alcohol and melted at 121°, with violent effervescence. A nitrogen determination agreed with the calculated for a dihydrochloride :



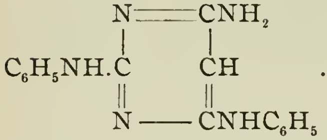
.2HCl.

	Calculated for $C_{11}H_{14}N_4SCl_2$.	Found. I.	Found. II.
N	18.36	18.01	18.11

The free pyrimidine base was obtained by triturating the hydrochloric acid salt with an excess of dilute sodium hydroxide. The base crystallized from benzene in clusters of microscopic prisms and melted at 124°, without effervescence, to a clear oil. It gave a strong test for sulphur, but contained no chlorine. Analysis (Kjeldahl) :

	Calculated for $C_{11}H_{12}N_4S$.	Found.
N	24.13	23.82

2,4-Dianilido-6-aminopyrimidine,

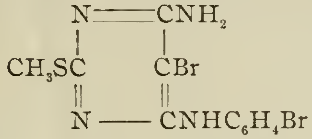


.—Seven grams of 2-methylmercapto-4-chlor-6-aminopyrimidine were heated with 2 molecular proportions of aniline, at 140°–150°, for 10 hours. A slow effervescence took place and methylmercaptan was constantly given off. Upon cooling, the reaction-product hardened to an amorphous solid. This was treated with a warm solution of sodium hydroxide, when it melted to a heavy, thick oil. The excess of aniline was then removed by distillation with steam. On cooling, a crystalline cake remained, which weighed 10 grams. This pyrimidine was very difficult to purify. It was extremely soluble in cold alcohol, benzene and ether. It dissolved in hot water, but separated, on cooling, as an oil which finally solidified to a hard, amorphous mass. To effect purification it was converted into its sulphuric acid salt. This salt is insoluble in cold water. When warmed with water it dissociates into the free base and sulphuric acid. It can be crystallized from alcohol containing free sulphuric acid. It separated from alcohol in granular crystals and melted at 190°-193°, with effervescence. Analysis (Kjeldahl):

	Calculated for $C_{16}H_{15}N_5.H_2SO_4$.	Found.
N	18.66	18.73

The pyrimidine base was obtained from this sulphuric acid salt by warming with a dilute solution of ammonium hydroxide. It separated as an oil, which finally solidified on standing. After drying over sulphuric acid for 24 hours, it melted at 65°–70°, to a slightly turbid oil. It is extremely soluble in the ordinary organic solvents. Analysis (Kjeldahl):

	Calculated for $C_{16}H_{15}N_5$.	Found.
N	25.27	24.81



$$\begin{array}{lcl} N & = & CNH_2 \\ | & & | \\ CH_3SC & & CBr \\ \| & & \| \\ N & - & CNHC_6H_4Br \end{array}$$

2-Methylmercapto-4-parabromanilido-5-brom-6-aminopyrimidine, . — The 2-methylmercapto-4-anilido-6-aminopyrimidine was dissolved in glacial acetic acid and bromine carefully added, as long as the bromine color disappeared. Stout prisms separated immediately, which were difficultly soluble in acetic acid. They decompose, with violent effervescence, at about 290°, turning somewhat brown at 210°–220°. A nitrogen determination agreed with the calculated for the hydrobromic acid salt of a dibrom-substitution-product:

	Calculated for $C_{11}H_{11}N_4SBr_3$.	Found.
N	11.89	12.29

The pyrimidine base was obtained by treating the hydrobromic acid salt with a 10 per cent solution of sodium hydroxide. It melted at 202°, without effervescence, to a clear oil. A nitrogen determination agreed with the calculated for 2-methylmercapto-4-bromanilido-5-brom-6-aminopyrimidine:

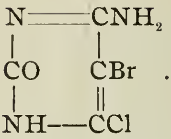
	Calculated for $C_{11}H_{10}N_4SBr_2$.	Found.
N	14.36	14.80

In order to establish the structure of this dibrompyrimidine derivative we have prepared it in the following manner: 3.6 grams of 2-methylmercapto-4-chlor-5-brom-6-aminopyrimidine were heated with 2.4 grams of parabromaniline, for 4 hours, at 120°–130°. A violet-colored oil was obtained which solidified on cooling. The material was insoluble in water, but soluble in hot acetic acid. In order to obtain the free base the substance was triturated with sodium hydroxide, filtered and then boiled in acetic acid, with animal charcoal, to remove the color. On cooling, long, slender prisms were obtained, which melted, without effervescence, at 202°. When some of this base was mixed with the above product, obtained by brominating 2-methylmercapto-4-anilido-6-aminopyrimidine (m. p.

202°), the melting-point was not lowered. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{10}N_4SBr_2$.	Found.
N	14.36	14.31

2-Oxy-4-chlor-5-brom-6-aminopyrimidine,



.—

This compound was obtained, in the form of its hydrobromic acid salt, when 2-oxy-4-chlor-6-aminopyrimidine was suspended in glacial acetic acid and treated with 1 molecular proportion of bromine. The hydrobromide separated as an orange-colored powder, which decomposed at 230°–240°, with effervescence. In order to obtain the free base the crude salt was warmed with a solution of dilute sodium hydroxide. When the alkali solution was acidified with dilute acetic acid the base separated as a crystalline precipitate. It crystallized from hot water in clusters of microscopic prisms and showed no definite melting-point, but began to turn brown at 210° and decomposed at about 230°, with violent effervescence. Analysis:

	Calculated for $C_4H_3ON_3ClBr$.	Found.
N	18.70	18.68

Action of Aqueous Ammonia on 2-Ethylmercapto-6-chlorpyrimidine.

At 140°–150°.—After heating with aqueous ammonia, for 4 hours, at 140°–150°, the pyrimidine was recovered unaltered.

At 185°–195°.—The chlorpyrimidine was heated with aqueous ammonia, for 3 hours, at 185°–195°. The ammoniacal solution was then evaporated to dryness. The crystalline residue was warmed with alcohol and filtered from the undissolved ammonium chloride. The alcoholic filtrate was then evaporated to dryness and the residue again dissolved in water. The chlorine was removed by precipitating with silver sulphate, then the sulphuric acid removed with barium hydroxide and the excess of barium with carbon dioxide. When the solution was evaporated to dryness we obtained a crystalline base which had all the properties of 2,6-diaminopyrimidine. It was extremely soluble in water. The base was identified by means of its platinum chloride salt. Analysis :

	Calculated for $(C_4H_5N_4)_2.H_2PtCl_6$.	Found.
Pt (194.8)	30.9	30.5

Action of Aqueous Ammonia on 2-Ethylmercapto-5-brom-6-chlorpyrimidine.[1]

At 140°–150°.—When the pyrimidine was heated with aqueous ammonia, at 140°–150°, for 4 hours, it was converted, quantitatively, into 2-ethylmercapto-5-brom-6-aminopyrimidine, melting sharply at 124°–125°.

At 185°–195°.—After heating for 4 hours, at 160°–170° and then for 3 hours, at 185°–195°, the 2-ethylmercapto-5-brom-6-aminopyrimidine was again obtained, melting at 124°–125°.

New Haven, Conn.,
May 1, 1905.

Contributions from the Sheffield Laboratory of Yale University.

CXXVI.—RESEARCHES ON PYRIMIDINES : 2-ETHYLMERCAPTO-5-AMINO-6-OXYPYRIMIDINE.

[ELEVENTH PAPER.]

By Treat B. Johnson.

The work described in this paper was undertaken with the object of investigating the formation and properties of 2-ethylmercapto-5-amino-6-oxypyrimidine. The examination of this pyrimidine was of particular interest in the study of oxydiaminopyrimidines, because it offered the possibility of synthesizing both 2,5-diamino-6-oxypyrimidine and 2-oxy-5,6-diaminopyrimidine. The preparation of 2,5-diamino-6-oxypyrimidine from this mercaptopyrimidine will be discussed in a later paper.

In a previous paper[2] from this laboratory, it was shown that ethyl formate condenses, in benzene, with ethyl hippurate, in the presence of metallic sodium, to form the sodium salt of formylethylhippurate.[1] This salt condensed very readily with pseudoethylthiourea to give the benzoyl derivative of 2-ethylmercapto-5-amino-6-oxypyrimidine. Attempts to hydrolyze this acyl derivative to the free pyrimidine, (V.), were unsuccessful. Acids could not be used for the hydrolysis on account of the ease with which the mercapto radical was displaced by hydroxyl. When boiled with sodium hydroxide the pyrimidine ring was opened, to form a sodium salt of α-benzoylamino-β-pseudoethylthioureaacrylic acid (I.). This acid was unstable and immediately condensed again to the pyrimidine, when the sodium salt was treated with acids :

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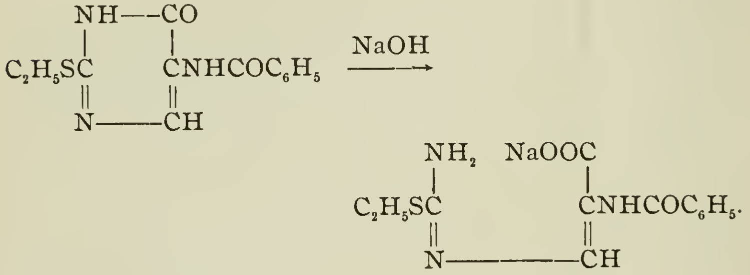
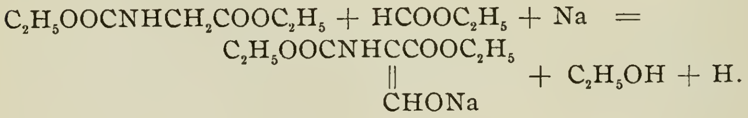
[1] Wheeler and Johnson : *Loc. cit.*

[2] Johnson and Clapp : This Journal, 32, 131 (1904).



I.

I now find that ethyl formate condenses very smoothly, in benzene, with carbethoxyaminoethylacetate, in the presence of metallic sodium, to form the sodium salt of formylcarbethoxyaminoethylacetate (II.) :



$$C_2H_5OOCNHCH_2COOC_2H_5 + HCOOC_2H_5 + Na = C_2H_5OOCNH\underset{\substack{\| \\ CHONa}}{C}COOC_2H_5 + C_2H_5OH + H.$$

II.

This sodium salt condensed at the ordinary temperature, in aqueous solution, with pseudoethylthiourea, giving α-carbethoxyamino-β-pseudoethylthioureaacrylic acid (III.). The yield of this acid corresponded to about 40–50 per cent of the theoretical :

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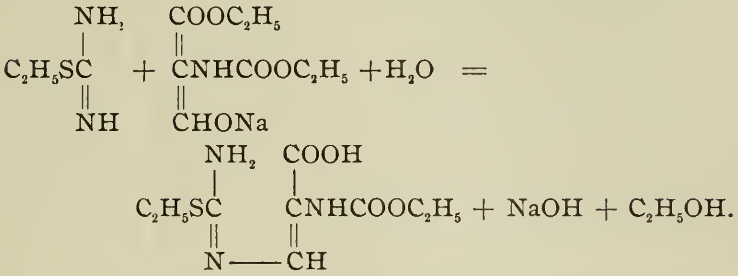
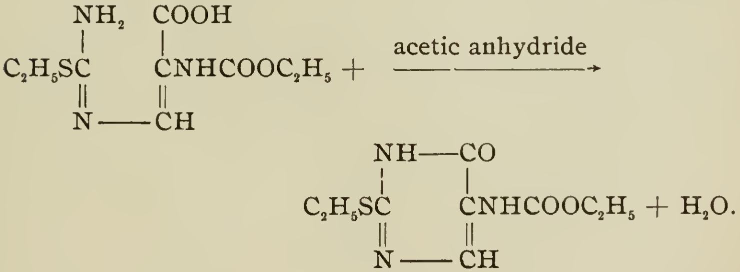
[1] Erlenmeyer, in his recent paper on the synthesis of serin and cystine, has shown that this salt can be obtained very smoothly by condensing ethyl formate with ethyl hippurate, in alcohol, by means of sodium ethylate. Ann. Chem. (Liebig), 337, 251.



$$\begin{array}{c}NH_2\\|\\C_2H_5SC\\\|\\NH\end{array} + \begin{array}{c}COOC_2H_5\\\|\\CNHCOOC_2H_5\\\|\\CHONa\end{array} + H_2O = \begin{array}{ccc}NH_2 & & COOH\\ | & & |\\ C_2H_5SC & & CNHCOOC_2H_5\\ \| & & \|\\ N & \text{——} & CH\end{array} + NaOH + C_2H_5OH.$$

III.

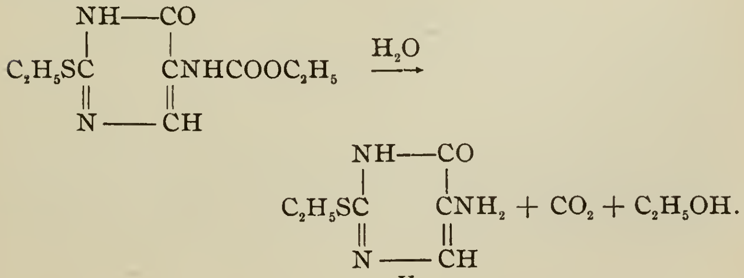
In no case have I succeeded in isolating the pyrimidine—2-ethylmercapto-5-carbethoxyamino-6-oxypyrimidine, (IV.)—as a product of this condensation. This compound, nevertheless, was easily obtained when the acrylic acid was warmed with acetic anhydride.



$$\begin{array}{ccc}NH_2 & & COOH\\ | & & |\\ C_2H_5SC & & CNHCOOC_2H_5\\ \| & & \|\\ N & \text{——} & CH\end{array} + \xrightarrow{\text{acetic anhydride}} \begin{array}{ccc}NH & \text{——} & CO\\ | & & |\\ C_2H_5SC & & CNHCOOC_2H_5\\ \| & & \|\\ N & \text{——} & CH\end{array} + H_2O.$$

IV.

When this pyrimidine, (IV.) was boiled with a solution of sodium hydroxide, it was converted into 2-ethylmercapto-5-amino-6-oxypyrimidine, (V.) :



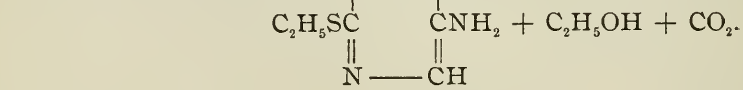
$$\begin{array}{ccc}NH & \text{——} & CO\\ | & & |\\ C_2H_5SC & & CNHCOOC_2H_5\\ \| & & \|\\ N & \text{——} & CH\end{array} \xrightarrow{H_2O} \begin{array}{ccc}NH & \text{——} & CO\\ | & & |\\ C_2H_5SC & & CNH_2\\ \| & & \|\\ N & \text{——} & CH\end{array} + CO_2 + C_2H_5OH.$$

V.

The formation of the above acrylic acid, (III.) is of interest as the second case in which the formation of intermediate products has been observed in the preparation of pyrimidines from pseudothioureas. The first case observed was described by Johnson and Clapp,[1] in a paper on the preparation of 2-amino-5-methyl-6-oxypyrimidine from guanidine and the sodium salt of formylethylpropionate. They not only observed the formation of an intermediate acrylic acid in this condensation, but also were able to show that it was capable of existing in two stereoisomeric modifications.

The α-carbethoxyamino-β-pseudoethylthiourea acrylic acid (III.) is especially characterized by its stability towards cold alkali solutions. On account of this pronounced stability I have designated it as the *trans*-modification. Under the experimental conditions I used I did not succeed in isolating an unstable *cis*-modification.

The *trans*-acid is very easily decomposed when boiled with strong and dilute solutions of sodium hydroxide. When it was boiled for a few minutes, with a strong sodium hydroxide solution and the solution then neutralized with acids or carbon dioxide, it was converted, almost quantitatively, into 2-ethylmercapto-5-amino-6-oxypyrimidine (V.):



$$\begin{array}{lll} & NH_2 & COOH \\ & | & | \\ C_2H_5S & C & C\,NHCOOC_2H_5 \\ & \| & \| \\ & N & -\!\!-\,CH \end{array} \xrightarrow{NaOH}$$

$$\begin{array}{lll} & NH & -\!\!-\,CO \\ & | & | \\ C_2H_5S & C & C\,NH_2 \\ & \| & \| \\ & N & -\!\!-\,CH \end{array} + C_2H_5OH + CO_2.$$

V.

This interesting saponification and condensation of the *trans*-acid to the mercaptoaminopyrimidine, (V.) led me to examine its behavior when warmed with a dilute solution of sodium hydroxide. The experimental data at hand seem to indicate that the *trans*-acid is saponified by dilute alkali to an intermediate 2-ethylmercapto-5-carboxylamino-6-oxypyrimidine, (VI.).

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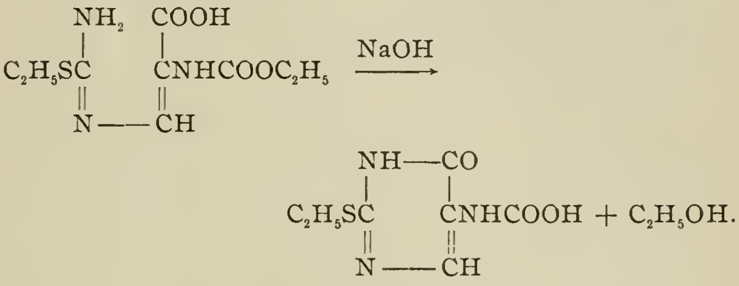
[1] *Loc. cit.*



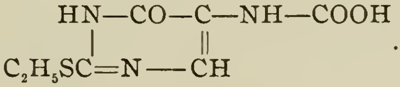
VI.

The existence of this intermediate carbamic acid is particularly interesting because of the fact that it contains a cyclic polypeptide linking. Analogous acids in the acyclic series have been obtained by Fisher,[1] in his important researches on polypeptides. The relationship between the above pyrimidine, (VI.) and a true polypeptide linking is made evident by the following comparison :

Acyclic series.

$$HN—CO—CH_2—NH—COOH.$$

Cyclic series.



It has been the usual experience, during the investigation of pyrimidines in this laboratory, to find that a mercaptooxypyrimidine reacts normally with phosphorus oxychloride, or phosphorus pentachloride, to give a chlorpyrimidine derivative. It has also been observed repeatedly that the resulting chlorpyrimidines are obtained combined with phosphorus oxychloride. These phosphorus compounds are very unstable and are decomposed by water, with formation of the free chlorpyrimidine. I now find that 2-ethylmercapto-5-amino-6-oxypyrimidine reacts with phosphorus oxychloride to form a phosphorus compound which is abnormally stable. The analytical determinations agree with the calculated for a phosphoryldichloride derivative (VII.):

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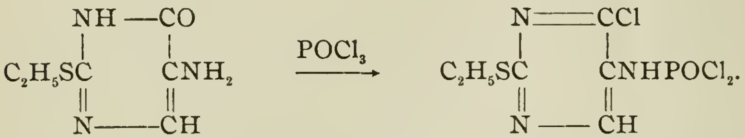
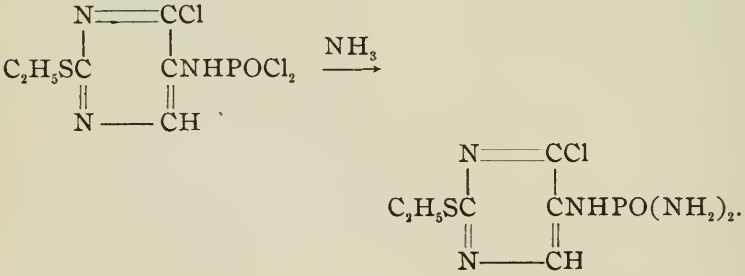
[1] Ber. d. chem. Ges., **36**, 2094 (1903).


VII.

This phosphorus derivative could be warmed with water without decomposition. When it was heated with alcoholic ammonia 2 chlorine atoms were removed and a stable compound was obtained, which I have, provisionally, represented as a phosphoryltriamide derivative,[1] (VIII.):


VIII.

The fact that this amino radical should show such pronounced affinity for phosphorus, is of interest. In a recent communication from this laboratory[2] it has been shown that the isomeric 2-ethylmercapto-4-oxy-6-aminopyrimidine reacts perfectly normally with phosphorus oxychloride, to form 2-ethylmercapto-4-chlor-6-aminopyrimidine, (IX.). Furthermore, Gabriel and

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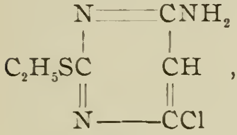
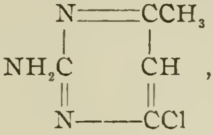
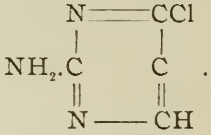
[1] These phosphoryl pyrimidine derivatives will receive further attention in this laboratory.

[2] Johnson and Johns: Preceding paper.

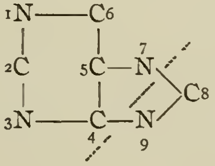
Colman[1] have shown that 2-amino-4-oxy-6-methylpyrimidine is converted, by phosphorus oxychloride, into 2-amino-4-chlor-6-methylpyrimidine. Later,[2] they observed that 2-amino-6-oxypyrimidine (isocytosine) also reacts normally with phosphorus oxychloride, to give 2-amino-6-chlorpyrimidine, (XI.).

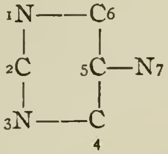

IX.


X.


XI.

In a previous publication on "Die Nucleinsaure des Weisenembryos," Osborne and Harris[3] have produced evidence to show that, in triticonucleic acid, there is a direct union between phosphorus and the nitrogen of the purine bases. Burian,[4] in a recent publication, has produced more evidence that supports the fact of this union in the nucleic acid molecule. Furthermore, his experiments tend to show that it is the nitrogen atom occupying position 7 in the purine molecule that is probably joined to the phosphorus. It is of interest to note, in this connection, that the nitrogen atom in the aminopyrimidine, (V.) which shows such affinity for phosphorus, corresponds to the nitrogen atom occupying position 7 in the purine molecule.





EXPERIMENTAL.

Sodium Salt of Formylcarbethoxyaminoethylacetate, $C_2H_5OOCNHC : (CHONa)COOC_2H_5$.—The carbethoxyaminoethylacetate, used for the preparation of this sodium salt, was prepared by Fisher's[1] method, from the hydrochloride of aminoethylacetate and chlorethylformate. The hydrochloride of aminoethylacetate was prepared according to Klages'[2] directions, from methyleneaminoacetonitrile. The method is extremely suitable for preparing large quantities of this hydrochloride. Ethyl formate condenses very smoothly with carbethoxyaminoethylacetate, in the presence of sodium, in either benzene or ether ; but it has been my experience that the condensation is much smoother and more rapid when benzene is used as the diluent. This sodium salt is much more stable in contact with the air than the sodium salt of formylethylacetate. I also found that the condensation could safely be accelerated by gently warming the benzene solution on the steam-bath. The purity of the salt obtained was not affected by this treatment. In all my condensations the yield of crude sodium salt has been about equal to the weight of carbethoxyaminoethylacetate used.

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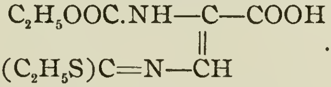
[1] Ber. d. chem. Ges., 32, 2921.

[2] *Ibid.*, 36, 3383.

[3] Z. physiol. Chem., 36, 85 (1902).

[4] Ber. d. chem. Ges., 37, 708.

Trans-α-carbethoxyamino-β-pseudoethylthiourea Acrylic Acid.



$$\begin{array}{l} C_2H_5OOC.NH{-}C{-}COOH \\ \qquad\qquad\qquad\quad \| \\ H_2N.(C_2H_5S)C{=}N{-}CH \end{array}$$

.—Twenty-five grams of the sodium salt of formylcarbethoxyaminoethylacetate were dissolved in water and added to an aqueous solution of pseudoethylthiourea, which was previously prepared by treating 17 grams of pseudoethylthiourea hydrobromide with 6 grams of potassium hydroxide. The clear solution, which resulted, was then allowed to stand for a few hours, at the ordinary temperature. Upon neutralizing with acetic acid a beautiful, white, crystalline compound separated. It was insoluble in alcohol and cold water. It could be dissolved, repeatedly, in cold solutions of sodium hydroxide and be precipitated, unaltered, by acids. It was purified for analysis by recrystallizing from hot water. It separated as a colorless powder, consisting of microscopic prisms. It showed no sharp melting-point but decomposed, with effervescence, at 259°. A yield of 11.5 grams of crude material was obtained. For analysis it was dried at 100°.

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[1] Ber. d. chem. Ges., **36**, 2107.

[2] *Ibid.*, **36**, 1508.

0.1574 gram substance gave 0.1341 gram $BaSO_4$ (Carius).

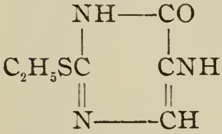
	Calculated for $C_9H_{15}O_4N_3S$.	Found.
N	16.00	15.75
S	12.25	11.70

The following table is given to show the comparative yields obtained in four different preparations of this *trans*-acid :

Table.

Weight of carbethoxyaminoethylacetate used. Grams.	Weight of sodium salt of condensation-product. Grams.	Weight of *trans*-acid. Grams.	Percentage of theoretical. Per cent.
30	32	11.0	40
20	25	11.5	46
40	45	20.0	45
40	45	19.5	44

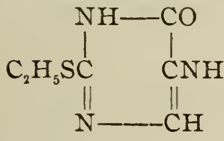
2-Ethylmercapto-5-carbethoxyamino-6-oxypyrimidine,



—This compound was easily obtained when the *trans*-acid, above described, was dissolved in warm acetic anhydride. On adding water the pyrimidine separated in prisms. It was easily purified by recrystallizing from 15 per cent acetic acid and separated, on cooling, in well-developed prisms, which melted, without effervescence, at 189°-190°, to a clear oil. The pyrimidine dissolves in sodium hydroxide solution and is reprecipitated, unaltered, by acids. It was also obtained, in an impure condition, when the *trans*-acid was boiled with glacial acetic acid. Analysis :

	Calculated for $C_9H_{13}O_3N_3S$.	Found.
N	17.28	17.35

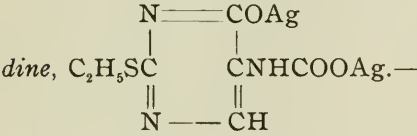
2-Ethylmercapto-5-amino-6-oxypyrimidine,



—Ten grams of the *trans*-acid were dissolved in 50 cc. of water, containing 5 grams of sodium hydroxide. The alkaline solution was boiled for about 20 minutes and then allowed to stand for 30 minutes. When the alkaline solution was made slightly acid with acetic acid the pyrimidine separated in beautiful, needle-like crystals, which melted, to a clear oil, at about 155°. It was purified by recrystallizing from hot water. It separated in clusters of radiating needles and, without effervescence, melted at 160°, to a clear oil. The yield was practically quantitative. This pyrimidine was also formed when 2-ethylmercapto-5-carbethoxyamino-6-oxypyrimidine was boiled with sodium hydroxide. Analysis (Kjeldahl):

	Calculated for $C_6H_9ON_3S$.	Found.
N	24.56	24.34

Disilver Salt of 2-Ethylmercapto-5-carboxylamino-6-oxypyrimidine,

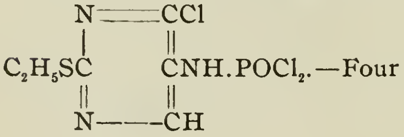


—The acid of this salt was obtained, in solution, from two different preparations of the *trans*-acid. It was formed by boiling the latter with a dilute solution of sodium hydroxide. It was very soluble in water and was not precipitated from the alkali solution by mineral acids or carbon dioxide. The disilver salt was obtained, after acidifying the alkaline solution with nitric acid, by adding a slight excess of 20 per cent silver nitrate solution. The salt was difficultly soluble in water and showed no crystalline form. Analysis of the substance, thoroughly dried over sulphuric acid:

0.1399 gram silver salt gave 0.0707 gram metallic silver.

	Calculated for $C_7H_7O_3N_3SAg_2$.	Found.
Ag	50.35	50.53

2-Ethylmercapto-5-phosphoryldichloramino-6-chlorpyrimidine,

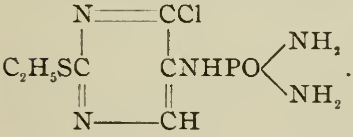


—Four and eight-tenths grams of

2-ethylmercapto-5-amino-6-oxypyrimidine were warmed, on a sand-bath, with an excess of phosphorus oxychloride. A reaction set in at once, with evolution of hydrochloric acid gas. After this ceased the excess of phosphorus oxychloride was removed by distillation under diminished pressure. I obtained a yellow, amorphous residue. When this was treated with water very little heat was evolved and a yellow, crystalline deposit remained suspended in the water. This residue was filtered and then warmed with water on the steam-bath, to destroy any phosphorus oxychloride. A thick, oily product, insoluble in water, was obtained by this treatment; it immediately solidified, on cooling, to a hard, crystalline cake. It was insoluble in the ordinary organic solvents and also in ammonium hydroxide. When treated with a solution of sodium hydroxide it showed a very peculiar behavior. The product was insoluble in sodium hydroxide, but gradually underwent decomposition and the solution assumed a dark green color. It gave strong tests for sulphur and phosphorus. It had no sharp melting-point, but decomposed at about 247°–250°. Analysis:

	Calculated for $C_6H_7ON_3SCl_3P$.	Found.
N	13.70	13.41

2-Ethylmercapto-5-phosphoryltriamino-6-chlorpyrimidine,



$$\begin{array}{lll} \mathrm{N} & \!\!=\!\!=\!\! & \mathrm{CCl} \\ | & & | \\ \mathrm{C_2H_5SC} & & \mathrm{CNHPO}\langle^{\mathrm{NH_2}}_{\mathrm{NH_2}} \\ \| & & \| \\ \mathrm{N} & \!\!-\!\!-\!\! & \mathrm{CH} \end{array}$$

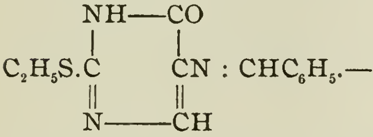
.—This complicated derivative was obtained when the above chloride was heated with alcoholic ammonia, for 3 hours, at 160°–165°. When the tube was opened there was no pressure and only a slight odor of mercaptan was noticeable. The pyrimidine was suspended in the alcohol and had a green, metallic appearance. It was insoluble in water and the ordinary organic solvents. It gave strong tests for chlorine, sulphur and phosphorus. It had no characteristic melting-point, but began to sinter at about 258° and decomposed at 290°–300°, according to the rate of heating. Analysis:

	Calculated for $C_6H_{11}ON_5SClP$.	Found.
N	26.16	26.12

Sodium Salt of α-Benzoylamino-β-pseudoethylthiourea Acrylic Acid, $H_2N(C_2H_5S)C : NCH : C(NHCOC_6H_5)COONa$.—This salt was obtained when 2-ethylmercapto-5-benzoylamino-6-oxypyrimidine[1] was boiled with a solution of sodium hydroxide. The sodium salt separated, on cooling, in needles. It crystallized from alcohol in needles and melted, with effervescence, at 124°–125°. When treated with acids it was converted into the unaltered pyrimidine, melting at 239°. Analysis .

	Calculated for $C_{13}H_{14}O_3N_3S.Na.H_2O$.	Found.
N	12.61	12.45

2-Ethylmercapto-5-benzalamino-6-oxypyrimidine,

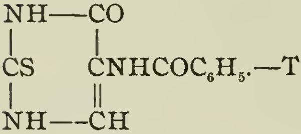


$$\begin{array}{lcl} & NH\text{---} & CO \\ & | & | \\ C_2H_5S.C & & CN : CHC_6H_5. \\ & \| & \| \\ & N\text{---} & CH \end{array}$$

—One gram of 2-ethylmercapto-5-amino-6-oxypyrimidine was warmed with 1 molecular proportion of benzaldehyde, for 1–2 hours, at 160°–180°. Water was given off immediately on warming and the material solidified to a crust in the hot bath. The pyrimidine crystallized from alcohol as a microscopic powder, from benzene in beautiful, rhombic plates or flattened prisms, melting at 185°–187°, to a clear oil. By prolonged boiling with water or dilute alcohol it was slowly decomposed into benzaldehyde and the unaltered pyrimidine. Analysis :

	Calculated for $C_{13}H_{13}ON_3S$.	Found.
N	16.21	16.00

2-Thio-5-benzoylamino-6-oxypyrimidine,



$$\begin{array}{ll} NH\text{---} & CO \\ | & | \\ CS & CNHCOC_6H_5. \\ | & \| \\ NH\text{---} & CH \end{array}$$

—Two grams of thiourea and 10 grams

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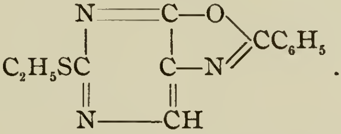
[1] Johnson and Clapp : *Loc. cit.*

of the sodium salt of formylethylhippurate[1] were dissolved in 50 cc. of water and warmed, on the steam-bath, for about 20 minutes. The solution assumed, at once, a turbid appearance, due to the separation of ethylhippurate. Upon cooling, a small amount of crystalline material separated from the alkaline liquid. This was removed by filtration and dried on the oven. No further precipitate was obtained when the alkaline solution was acidified with acetic acid. The crystalline product was purified by crystallizing from acetic acid. It separated in plates and decomposed at 300°–310°, according to the rate of heating. It was soluble in sodium hydroxide and was reprecipitated, unaltered, by acids. It was insoluble in water and alcohol. When it was boiled with hydrochloric acid it was decomposed with evolution of hydrogen sulphide. Analysis (Kjeldahl):

	Calculated for $C_{11}H_9O_2N_3S$.	Found.
N	17.00	16.86

2-Ethylmercapto-5,6-(μ-phenyloxazoline)pyrimidine (By S. H. Clapp),  .—Nine grams of 2-ethylmercapto-5-benzoylamino-6-oxypyrimidine[1] were heated to boiling with 50 cc. of phosphorus oxychloride, for 3 hours. Hydrochloric acid was evolved continuously. The excess of phosphorus oxychloride was then distilled off under diminished pressure. I obtained a thick varnish, which would not solidify. This was treated with cold water, to destroy any excess of phosphorus oxychloride. Heat was evolved and a white, crystalline solid separated. This was thoroughly washed with water and purified by recrystallizing from alcohol. It melted, without effervescence, at 108°–109° to a clear oil. It was free from chlorine. Analysis (Carius):

0.1399 gram substance gave 0.1268 gram $BaSO_4$.

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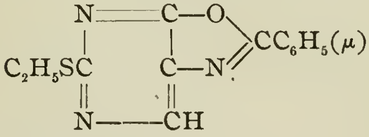
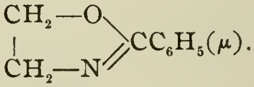
[1] Johnson and Clapp: *Loc. cit.*

	Calculated for $C_{13}H_{11}N_3OS$.	Found.
S	12.45	12.43

The compound was insoluble in sodium hydroxide and could be boiled with alkali without decomposition. When warmed for a short time with hydrochloric acid it was converted into the unaltered 2-ethylmercapto-5-benzoylamino-6-oxypyrimidine, melting at 238°–239°. When it was suspended in dry benzene and the benzene saturated with dry hydrochloric acid gas, the hydrochloride was formed, melting, with violent effervescence, at 147°. When this salt was warmed with water it underwent dissociation and the oxazoline was recovered. Some of the hydrochloric acid salt was heated in a sealed tube, with alcoholic ammonia, for 2 hours, at 100°–110°. The alcoholic solution was evaporated to dryness and then treated with water, to remove ammonium chloride. The insoluble residue proved to be the unaltered oxazoline, melting at 108°–109°.

The close relationship between our oxazoline and μ-phenyloxazoline, which was prepared by Gabriel and Heyman,[1] is shown by the following formulæ:





New Haven, Conn.,
May 6, 1905.

Contributions from the Chemical Laboratory of Harvard College.

THE DETERMINATION OF PHOSPHORIC ACID BY MEANS OF AMMONIUM PHOSPHOMOLYBDATE.

[SECOND PAPER.]

By Gregory Paul Baxter and Roger Castle Griffin.

In a previous paper by one of us,[2] it was shown that the precipitate, formed by adding a solution of phosphoric acid to a solution of an excess of molybdic acid, never possesses the formula usually assigned to it, $(NH_4)_3PO_4 12MoO_3$, but that, when washed with a solution of ammonium nitrate and heated to 300°, it always contains a greater or less excess of MoO_3 over that required by the above formula, owing to occlusion of either molybdic acid or ammonium molybdate. The extent of this occlusion was found, however, to be constant under given conditions of precipitation, so that the weight of the precipitate may be used for the estimation of phosphoric acid, provided the formulæ of the precipitates formed under various conditions are known. Finally, the compositions of precipitates formed in the presence of varying amounts of molybdic acid and ammonium nitrate were given.

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[1] Ber. d. chem. Ges., **23**, 2495.

[2] Baxter: This Journal, **28**, 298 (1902).

In the first investigation, the extent of the occlusion was found to increase with increasing concentration of ammonium salts and with decreasing acid concentration, hence the conclusion was drawn that the substance occluded is ammonium molybdate and not molybdic acid. Since the Pemberton method for the determination of phosphoric acid involves the titration of ammonium phosphomolybdate with standard alkali, it is of considerable importance to obtain more conclusive evidence as to the nature of the occluded substance. Such evidence is presented in this paper and the fact is established that both ammonium molybdate and molybdic acid are occluded, the latter in larger quantities under the usual conditions of precipitation.

Since it was not determined, in the earlier investigation, whether precipitates formed in hot solutions, or by pouring molybdic acid solutions into phosphate solutions, were of the same composition as those obtained by adding phosphoric acid to molybdic acid in the cold, these points were considered first.

A solution of disodium phosphate was prepared of such a strength that 50 cc. contained about 0.1 gram of P_2O_5. This solution was then analyzed, according to the method described in the above-mentioned paper, as follows: Portions of exactly 50 cc. of the phosphate were poured, with constant stirring, into 100 cc. portions of the standard molybdic solution.[1]

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[1] *Loc. cit.*, p. 300.

The precipitates were allowed to stand about 18 hours and then, after washing with a 10 per cent solution of ammonium nitrate, they were collected upon weighed Gooch crucibles. Finally, they were heated in an electric air-bath, at 300°–315°, for 2 hours and weighed. At this temperature the adhering ammonium nitrate is completely decomposed and constant weight attained. Precipitates formed in this way have been shown to contain 3.742 per cent of P_2O_5.[1] As a check upon the accuracy of these experiments, two analyses were made in which 10 grams of ammonium nitrate were added to the molybdic acid solution before precipitation and two where 200 cc. of molybdic acid were employed. The precipitates, in these cases, contained 3.739 and 8.728 per cent of P_2O_5, respectively.[2]

Table I.

Number of analysis.	Molybdic acid. cc.	Ammonium nitrate. Grams.	Weight of precipitate. Grams.	Weight of P_2O_5. Gram.
1	100		2.6655	0.09974
2	"		2.6614	0.09959
3	"		2.6648	0.09972
4	"		2.6626	0.09964
5	"	10	2.6662	0.09969
6	"	10	2.6631	0.09958
7	200		2.6723	0.09960
8	"		2.6724	0.09960
			Average,	0.09965

If precipitation is carried out in the reverse fashion, by pouring the molybdic acid into the phosphate, either inclusion or occlusion of the phosphate by the phosphomolybdate might be expected, with the result that the weight of the precipitate would be considerably too small. Furthermore, the composition of the precipitate, formed under these conditions, might be different from that of the compound produced when the phosphate is added to the molybdic acid. In analyses 9 to 12 the molybdic acid was added rapidly, with vigorous stirring, to the phosphate. The precipitates, when treated as before, varied in weight considerably, as might be expected, but weighed slightly more, instead of less than those obtained by the reverse fashion of precipitation. To determine whether the rate of precipitation had any influence upon the weight of the precipitate, in analyses 13 to 15 the molybdic acid was added, very slowly, from a large thistle tube with a capillary outlet. The results of these experiments were not materially different from those of rapid precipitation.

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[1] *Loc. cit.*, p. 303.

[2] *Ibid.*, p. 314.

A repetition of these analyses, with 200 cc. of molybdic acid and in the presence of much ammonium nitrate, gave similar results. Evidently precipitates formed by adding molybdic acid to phosphoric acid solutions are too variable in composition to be suitable for exact quantitative work.

Table II.

Number of analysis.	Molybdic acid. cc.	Ammonium nitrate. Grams.	Rate of precipitation.	Weight of precipitate. Grams.	Calculated weight of precipitate. Grams.	Difference. Gram.
9	100		Rapid	2.6754	2.663	0.012
10	"		"	2.6678	"	0.005
11	"		"	2.6630	"	0.000
12	"		"	2.6660	"	0.003
13	"		Slow	2.6615	"	—0.001
14	"		"	2.6689	"	0.006
15	"		"	2.6762	"	0.013
16	200		Rapid	2.6768	2.673	0.004
17	"		"	2.6898	"	0.017
18	"		"	2.6758	"	0.003
19	"		Slow	2.6705	"	—0.002
20	"		"	2.6785	"	0.006
21	100	10	Rapid	2.6721	2.665	0.007
22	"	10	"	2.6659	"	0.001
23	200	10	"	2.6700	2.677	—0.007

It may be added that all the precipitates formed by pouring the molybdic acid into the phosphate showed a much greater tendency to adhere tenaciously to the beaker than those precipitated in the reverse fashion. Several analyses were lost through inability to remove the precipitate from the glass even by the most vigorous rubbing with a rubber "policeman."

The usual directions for the determination of phosphoric acid with molybdic acid advocate precipitation in warm solution, for precipitation in warm or hot solution is completed more rapidly than in cold solution and, furthermore, has the advantage that the precipitate is more highly crystalline and, therefore, may be more easily manipulated. To determine whether the composition of the precipitate is affected by the temperature, experiments were carried out as follows: In analyses 24 and 25 both molybdic acid and phosphate were heated to 50° and then the phosphate was added to the molybdic acid. The precipitates were maintained at 50°–60° for nearly 4 hours and were then washed with ammonium nitrate and collected. In one experiment, where filtration took place after only 1½ hours, precipitation was incomplete. In analysis 26 precipitation took place at room temperature and the precipitate was digested for nearly 4 hours, at 50°–60°.

Table III.

Number of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Calculated weight of precipitate. Grams.	Difference. Gram.
24	100	2.6890	2.663	0.023
25	200	2.7019	2.673	0.029
26	100	2.6765	2.663	0.014

All three results show that the extent of the occlusion is greater at high temperatures than at low and analysis 26 indicates that occlusion may take place after precipitation, as was pointed out in the previous paper.[1] Since the occlusion probably varies considerably with the temperature and period of heating, high temperatures should be avoided in the precipitation of ammonium phosphomolybdate, if the precipitate is to be weighed.

The question as to whether ammonium phosphomolybdate occludes molybdic acid or ammonium molybdate was somewhat difficult to settle. Since, as has already been said, the extent of the occlusion increases with increasing concentration of ammonium salts and with diminishing acid concentration, it seems probable that ammonium molybdate and not molybdic acid is carried down. Much more conclusive evidence, however, would be afforded by a direct determination of either the free molybdic acid or the ammonia in the precipitate.

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[1] *Loc. cit.*, p. 312.

At first the attempt was made to determine the free molybdic acid by dissolving the precipitate in half-normal potassium hydroxide and titrating the excess of alkali with standard acid, in the presence of phenolphthalein. The precipitate was not ignited before the titration, since the occluded substance, whether ammonium molybdate or molybdic acid, is converted into molybdic trioxide at 300°. Qualitatively this method was successful, although the end-point with phenolphthalein, in the presence of ammonia, is not at all sharp.

Fifty cc. portions of a sodium phosphate solution, containing 0.1018 gram of phosphorus pentoxide, were precipitated by addition to 100 cc. and 200 cc. portions of molybdic acid. The precipitates were allowed to stand some time and then were washed thoroughly, by decantation, with a 5 per cent solution of ammonium nitrate and were freed, as far as possible, from the washing solution by suction upon a Gooch crucible. Next the precipitates were transferred with water to beakers, dissolved in a slight excess of half-normal potassium hydroxide, which had been freed from carbonate by means of a slight excess of barium hydroxide and, finally, the excess of hydroxide was determined by titration with standard acid, in the presence of phenolphthalein. Since all the precipitates contained exactly the same amount of phosphorus pentoxide, the slightly larger volumes of alkali required by the precipitates obtained with 200 cc. of molybdic acid point to the presence of more occluded molybdic acid in these precipitates than in those formed with 100 cc. of molybdic acid. It is noticeable also that the quantities of hydroxide used correspond much more nearly to the requirement of 48 molecules of potassium hydroxide than to that of 46 molecules, for each molecule of phosphorus pentoxide. Assuming that, in the titration, the neutral point with phenolphthalein is reached when the neutral molybdate and the dimetallic phosphate have been produced, the formula of the precipitate must be

$$(NH_4)_2HPO_4 12MoO_3 \quad \text{and not} \quad (NH_4)_3PO_4 12MoO_3,$$

as is usually assumed.

Table IV.

Number of analysis.	Molybdic acid. cc.	Weight of P_2O_5. Gram.	N/2 KOH used. cc.	Theory for 46 molecules KOH. cc.	Theory for 48 molecules KOH. cc.
27	100	0.1018	67.81	65.97	68.94
28	"	"	68.40	"	"
29	200	"	68.65	"	"
30	"	"	68.27	"	"

In order to avoid the uncertainty of the phenolphthalein end-point, an attempt was made to perform the titrations with methyl orange, by first removing the weak phosphoric and molybdic acids with barium chloride, after solution of the phosphomolybdate in standard alkali. Although, as in the previous experiments, it was evident that more alkali was required for precipitates formed with a large excess of molybdic acid than with a small excess, no more satisfactory quantitative results were obtained than in the previous case, owing, apparently, to the fact that the precipitated barium phosphate and molybdate were not of constant composition.

Attention was next turned to the more promising problem of the determination of the ammonia in the precipitate. If the occluded substance is molybdic acid, the relation of the ammonia to the phosphorus pentoxide should be constant under all conditions of precipitation, while, if ammonium molybdate is occluded, the ratio of ammonia to phosphoric acid will increase with increasing occlusion. Obviously, a washing solution must be obtained which contains no ammonium salts. Since water decomposes the precipitate and since nitric acid dissolves it appreciably, potassium nitrate was first chosen for the purpose. In order to show that ammonium phosphomolybdate is not appreciably soluble in this medium, several precipitates, formed in the usual way, were washed with a 10 per cent solution of potassium nitrate. When the washings were treated with a large excess of molybdic acid, they remained perfectly clear and colorless. Moreover, when these precipitates were further washed with 10 per cent ammonium nitrate solution, collected and weighed, they were almost absolutely identical in weight with those where the potassium nitrate treatment was omitted.

Table V.

Number of analysis.	Molybdic acid. cc.	Weight of precipitate. Grams.	Calculated weight of precipitate. Grams.
31	100	2.6715	2.676
32	"	2.6787	"
33	"	2.6732	"

The per cent of ammonia in precipitates formed in the usual way was determined as follows: They were first washed with 10 per cent potassium nitrate solution and collected upon Gooch crucibles. Then they were transferred to a retort with water. By means of a rubber stopper a dropping funnel was fitted to the tubulature of the retort, through which concentrated potassium hydroxide was introduced. Finally, the ammonia was distilled into N/10 hydrochloric acid. A very small negative correction was necessary on account of the use of rubber in the distilling apparatus. This correction was determined by blank experiments:

Table VI.

Number of analysis.	Weight of precipitate calculated. Grams.	Weight of P_2O_5 calculated. Gram.	N/10 HCl used. cc.	Per cent of ammonia.	Molecules of ammonia for 1 molecule of P_2O_5.
34	2.676	0.1001	11.80	0.752	1.67
35	"	"	13.02	0.830	1.84
36	"	"	10.43	0.665	1.48

It was evident that either ammonium phosphomolybdate contains very much less ammonium than is usually supposed, or else the ammonium in the precipitate had been replaced by the potassium of the washing solution. The latter explanation proved to be the correct one, for in an experiment where a similar precipitate was washed with potassium nitrate and then allowed to stand in contact with potassium nitrate for about a day, the per cent of ammonia was found to be 0.44, which corresponds to 0.98 molecule of ammonia for each molecule of phosphorus pentoxide and in another, where the precipitate stood under 10 per cent potassium nitrate for 3 weeks, with occasional replacement with fresh solution, the per cent of ammonia was only 0.13, corresponding to 0.28 molecule of ammonia.

Since potassium is heavier than ammonium, it might be expected that the precipitates in analyses 31 to 33, where potassium had replaced ammonium to a considerable extent, would have been heavier than those which had been washed with ammonium nitrate only. Evidently, however, the potassium, in the presence of a high concentration of ammonium, is as easily replaced by ammonium. Hence the precipitates in question, after the final washing with ammonium nitrate to which they were subjected, contained little potassium and the results were the same as if the potassium nitrate treatment had been omitted.

A final attempt to determine the ammonia content was then made in the following way: Precipitates of the phosphomolybdate were collected upon Gooch crucibles, after being washed with 1 per cent nitric acid. Since a small portion of the precipitate was dissolved by the nitric acid, the filtrates were treated with a large amount of molybdic acid and were allowed to stand over night, to insure complete precipitation of the dissolved phosphomolybdate. The weight of this small amount of precipitate was determined and, in the calculations, was subtracted from the theoretical weight of the ignited precipitate. The main precipitate was transferred to a retort and the ammonia determined as described above. Although the dissolved phosphomolybdate was precipitated from the filtrate and washing solution in the presence of a much larger excess of molybdic acid than the main bulk of the precipitate, the weight of the dissolved substance was so small, between 0.0000 and 0.0180 gram, that the different conditions of precipitation could not have affected the weight of the whole precipitate to an extent greater than a few thousandths of a per cent.

Table VII.

Number of analysis.	Molybdic acid. cc.	Weight of precipitate calculated. Grams.	Weight of P_2O_5 calculated. Gram.	N/10 HCl used. cc.	Per cent of ammonia.	Molecules of ammonia for P_2O_5.
37	100	2.7121	0.1015	29.98	1.881	4.20
38	“	2.6802	0.1003	29.48	1.872	4.17
39	“	2.7188	0.1017	30.71	1.922	4.29
40	200	2.7200	0.1014	28.78	1.801	4.03
41	“	2.7245	0.1016	29.89	1.867	4.18
42	“	2.7300	0.1018	29.86	1.862	4.17
43	“	2.1640	0.0807	23.11	1.818	4.07
44	“	2.7175	0.1013	28.44	1.791	3.99

Since ammonium phosphomolybdate is always precipitated in the presence of much nitric acid, it is extremely probable that its composition was not changed during the washing with dilute nitric acid. Consequently, there can be no doubt, from the above results, that in ammonium phosphomolybdate only 2 of the hydrogens of phosphoric acid are replaced by ammonium and that its formula is, approximately, $(NH_4)_2HPO_4 12MoO_3$. This is to be expected, however, from the fact that ammonia is a very weak base and phosphoric acid a very weak acid, so that the tertiary ammonium phosphate should be largely hydrolyzed in water solution and, in strongly acid solution, would be chiefly converted into molecular phosphoric acid. This conclusion is borne out by some unpublished experiments by Professor C. R. Sanger, in this laboratory, in which he found that triammonium phosphate is too unstable to be obtained in the solid state, from solution and that even the diammonium phosphate readily parts with a considerable portion of its ammonia.

In Table VII. the small excess over 4 molecules of ammonia for every molecule of phosphorus pentoxide is undoubtedly due to occluded ammonium molybdate. In the previous paper[1] it was shown that, in precipitates formed with 100 cc. of molybdic acid for 0.1 gram of phosphorus pentoxide, the excess of molybdic trioxide, over that theoretically necessary from the formula $(NH_3)_3PO_4 12MoO_3$, was 1.08 per cent, which, in the form of ammonium molybdate, corresponds to 0.52 molecule of ammonia for every molecule of phosphorus pentoxide. Evidently the occluded substance is chiefly molybdic acid, since the excess actually found is only about 0.2 of a molecule. The slightly smaller excess in the precipitates formed with the larger quantities of molybdic acid, although the precipitates themselves are heavier, indicates less occlusion of ammonium molybdate but greater occlusion of molybdic acid. Doubtless this is due to the fact that, if a small excess of molybdic acid is employed, the acidity of the solution is diminished to a much greater extent by the formation of the precipitate, owing to its strongly acid nature, than when a large excess of molybdic acid is used. If, moreover, the acid concentration should be still further diminished by the use of a lower concentration of nitric acid in the molybdic acid solution, a still larger proportion of occluded ammonium molybdate is to be expected. This expectation was fulfilled in the following experiments. Precipitates were produced with the use of a molybdic acid solution containing one-half the usual concentration of nitric acid. These were washed with nitric acid and analyzed for ammonia as before. Under these conditions more than half the occluded substance was found to be ammonium molybdate.

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[1] *Loc. cit.*, p. 305.

Table VIII.

Number of analysis.	Molybdic acid. cc.	Weight of precipitate calculated. Grams.	Weight of P_2O_5 calculated. Gram.	N/10 HCl used. cc.	Per cent of ammonia.	Molecules of ammonia for P_2O_5.
45	100	2.7492	0.1040	31.65	1.964	4.32
46	"	2.7623	0.1045	31.69	1.957	4.36

These results, as well as those recorded in Table VII., are in decided conflict with analyses made in the previous research, where the percentages of ammonia, in precipitates which had been washed with ammonium nitrate and then heated to 300°, were found to be from 2.627 to 2.665, corresponding to about 6 molecules of ammonia for each molecule of phosphorus pentoxide. However, it was impossible, by suction upon Gooch crucibles, completely to free the precipitates from the ammonium nitrate solution used in the washing and, since the precipitates were then heated to 300° while still moistened with the ammonium nitrate, it is evident that during the ignition the third hydrogen of the phosphoric acid was replaced by the ammonium from this ammonium nitrate.

In order to weigh precipitates in which it was impossible that this replacement of hydrogen by ammonium could have taken place, experiments were performed with the use of 1 per cent nitric acid, instead of ammonium nitrate, as the washing solution. The precipitates were collected upon Gooch crucibles and heated to 300°, as already described. The filtrates and wash-waters were carefully preserved and the dissolved phosphomolybdate was determined as on page 212. Although the small quantity of precipitate, obtained from the filtrate and wash-waters, was of somewhat different composition from the main bulk of the precipitate, this difference could not have produced an error of more than 0.1 or 0.2 of a milligram.

Table IX.

Number of analysis.	Molybdic acid. cc.	Weight of main precipitate. Grams.	Weight of precipitate from filtrate. Gram.	Total weight of precipitate. Grams.
47	100	2.6808	0.0082	2.6890
48	"	2.6757	0.0118	2.6875
49	"	2.6816	0.0091	2.6907
			Average,	2.6891

Precipitates prepared in exactly the same manner, but washed with ammonium nitrate, weighed, on an average, 2.7223 grams. Such precipitates have been shown to contain 1.08 per cent excess of molybdic trioxide, owing to occlusion, which corresponds to 0.286 molecule of molybdic trioxide for each molecule of phosphorus pentoxide, hence they have the formula $(NH_4)_3PO_4 12.143MoO_3$. The precipitates obtained as those in Table IX. should, then, have the formula $(NH_4)_2HPO_4 12.143MoO_3$ and should weigh 2.698 grams, which is slightly more than that actually found. The previous conclusion, that the precipitate formed by the addition of a phosphate to a solution of molybdic acid is the diammonium phosphomolybdate is thus supported.

Summary.

The results of this investigation are as follows :

1. The conclusion reached in the previous paper is confirmed, that it is possible to obtain ammonium phosphomolybdate constant in composition and in a state suitable for weighing, so that it may be used for the accurate estimation of phosphoric acid.

The composition of the precipitate varies with the excess of molybdic acid, however, hence the excess of precipitant must be known. For the composition of the precipitate under different conditions the previous paper should be consulted. Attention is called to an obvious typographical error in the diagram on p. 314 of that paper, where the fourth abscissa should be 3.735 instead of 3.730.

The precipitate must be formed by pouring the phosphate into the molybdic acid. If the precipitation is performed in the reverse manner the composition of the precipitate varies considerably.

The precipitation should be performed at room temperature. At higher temperatures occlusion is increased.

2. The ammonium in the precipitate is readily replaced by potassium, in the presence of a high concentration of potassium salts, but the reverse change takes place if the potassium phosphomolybdate is then treated with concentrated ammonium salts.

3. The precipitate of ammonium phosphomolybdate is the diammonium salt.[1] When heated to a high temperature with ammonium nitrate it is converted, almost wholly, into the triammonium phosphomolybdate.

[1] Gibbs found only 5 molecules of ammonia for each molecule of phosphorus pentoxide. THIS JOURNAL, 3, 324 (1881).

4. Ammonium phosphomolybdate occludes varying amounts of both molybdic acid and ammonium molybdate, according to the conditions of precipitation.

5. The Pemberton method for the determination of phosphoric acid, by titration of ammonium phosphomolybdate with standard potassium hydroxide, is incapable of giving accurate results for several reasons. In the first place, 24 molecules of alkali are required for the neutralization of 1 molecule of ammonium phosphomolybdate and not 23, as is commonly assumed. Secondly, ammonium phosphomolybdate occludes varying amounts of molybdic acid. Finally, the titration with phenolphthalein, in the presence of ammonia, always yields uncertain results.

6. No method for estimating phosphoric acid, which depends upon the determination of the molybdic acid in ammonium phosphomolybdate, is accurate unless allowance is made for the occluded ammonium molybdate and molybdic acid.

Cambridge, Mass.,
April 26, 1905.

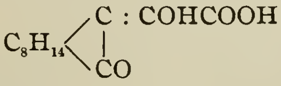
CONDENSATION COMPOUNDS OF CAMPHOROXALIC ACID AND AMINES.

[SEVENTH COMMUNICATION ON CAMPHOROXALIC DERIVATIVES.[1]]

By J. Bishop Tingle and William Edwin Hoffman, Jr.

THEORETICAL.

The investigations carried out by J. Bishop Tingle and his co-workers have shown, almost conclusively, that the condensation compound of camphor and ethyl oxalate, which has been termed camphoroxalic acid, is an unsaturated keto-alcohol,



and not the 1,3-diketone,

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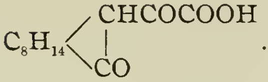
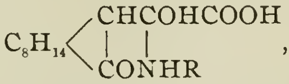
[1] The previous papers on this subject are as follows: Inaug. Diss., Munich, 1889, p. 34. J. Chem. Soc., **57**, 652 (1890). This Journal, **19**, 393 (1897); **20**, 318 (1898); **21**, 238 (1899); **23**, 214 (1900). J. Am. Chem. Soc., **23**, 363 (1901).



$$C_8H_{14}\left\langle\begin{array}{l}CHCOCOOH\\ |\\ CO\end{array}\right. .$$

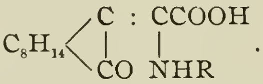
In the course of the work, a new class of compounds was discovered, formed by the condensation of the acid with amines.[1]

The condensation compounds of the sodium and potassium salts of camphoroxalic acid and of the ethyl ester with amines, both aliphatic and aromatic, were studied. The primary products, in all cases, were, apparently, additive substances of the general type,



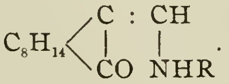
$$C_8H_{14}\left\langle\begin{array}{l}CHCOHCOOH\\ |\quad\ |\\ CONHR\end{array}\right. ,$$

but only one compound with this formula could be isolated. It was obtained from hydroxylamine and sodium camphoroxalate, the other substances appeared to be unstable and eliminated the elements of water, giving rise to products of the general formula :



$$C_8H_{14}\left\langle\begin{array}{ll}C & :\ CCOOH\\ | & \quad\ |\\ CO & \ NHR\end{array}\right. .$$

Compounds of this nature were prepared from ammonia, hydroxylamine, semicarbazine, aniline and α- and β-naphthylamine. Such substances as those formulated above might be expected to undergo further change ; carbonic anhydride might be evolved with the formation of a compound of the type :



$$C_8H_{14}\left\langle\begin{array}{ll}C & :\ CH\\ | & \quad |\\ CO & \ NHR\end{array}\right. .$$

In addition to the above, a third compound of the amine with camphoroxalic acid might be formed, namely, a salt of the acid mentioned above ; this would be represented by the formula :

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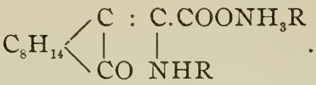
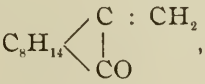
[1] J. Am. Chem. Soc., **23**, 363 (1901).



$$C_8H_{14}\Big\langle\begin{matrix}C & : & C.COONH_3R\\ | & & |\\ CO & & NHR\end{matrix}\quad .$$

Representatives of these various types were actually prepared from aniline and sodium camphoroxalate. The first by the action of the constituents in a neutral solvent, at the ordinary temperature; the second by the action of aniline and camphoroxalic acid, under pressure, at 130°, or by heating the first compound above its melting-point. The third derivative was obtained by the action of aniline on free camphoroxalic acid, in a neutral solvent, at the ordinary temperature.

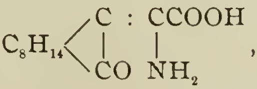
In naming these compounds the simplest and most advisable method appeared to be to regard them as derived from the complex,



$$C_8H_{14}\Big\langle\begin{matrix}C & : & CH_2\\ | & & \\ CO & & \end{matrix}\quad ,$$

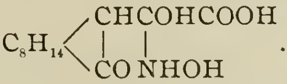
for which the term camphoformene was suggested; it is self-explanatory and indicates the presence of the double linkage.

By the action of ammonia on sodium or potassium camphoroxalate, sodium or potassium camphoformeneaminecarboxylate was obtained, from which the free acid,



$$C_8H_{14}\Big\langle\begin{matrix}C & : & CCOOH\\ | & & |\\ CO & & NH_2\end{matrix}\quad ,$$

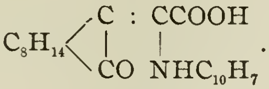
was isolated. Sodium camphoroxalate combines with hydroxylamine, forming the compound



$$C_8H_{14}\Big\langle\begin{matrix}CHCOHCOOH\\ |\quad\ |\qquad\qquad\\ CO\ NHOH\qquad\end{matrix}\quad .$$

Semicarbazine unites with potassium or sodium camphoroxalate under the same conditions as hydroxylamine. The products were thought to consist of two compounds having, apparently, the same empirical formula, but differing in their behavior toward solvents.

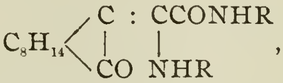
α-Naphthylamine reacted with sodium camphoroxalate, under somewhat similar conditions to aniline and formed α-naphthylcamphoformeneaminecarboxylic acid. The corresponding derivative of β-naphthylamine was also obtained :



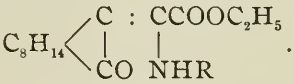
The interaction of orthophenylenediamine and sodium camphoroxalate produced camphoquinoxaline, $C_{18}H_{20}N_2O_2$.

ETHYL CAMPHOROXALATE DERIVATIVES.

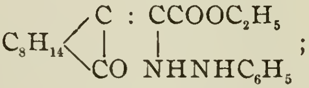
Methylamine, ethylamine, semicarbazine, aniline and ammonia condensed with ethylcamphoroxalate to form compounds of the general formula,



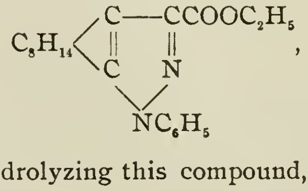
while, with aniline or β-naphthylamine, the product has the formula



Phenylhydrazine reacted with ethyl camphoroxalate forming



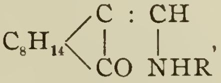
when this was heated above its melting-point ethyl camphylphenylpyrazolcarboxylate,



results and, on hydrolyzing this compound, the free acid was obtained.

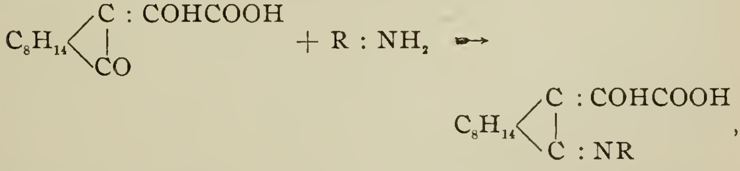
Condensation compounds could not be isolated from ethyl camphoroxalate or sodium camphoroxalate with para- and metaphenylenediamine, ethylaniline and dimethylaniline.

The object of the present investigation was to determine, if possible, what action would take place between the free camphoroxalic acid and aliphatic and aromatic amines. To ascertain, as far as we were able, the limits within which the condensation takes place, to endeavor to find the cause of the inhibition of the reaction with some amines, whether it was due to stereometrical influences, to the aliphatic or aromatic nature of the amine, or to its more or less strongly developed positive properties and to try to discover the conditioning factors for the production of substances of the varying types referred to in the preceding pages. The action of camphoroxalic acid upon a number of metallic compounds was also investigated and the typical salts of camphoroxalic acid, described below, have been prepared and analyzed. Finally, we desired to investigate the action of acylhalides or substituted acylhalides upon compounds of the type,



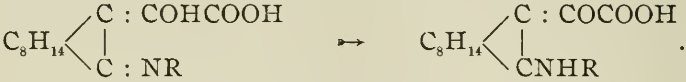
$$C_8H_{14}\left\langle\begin{array}{ll} C & : CH \\ | & \;\;\;| \\ CO & NHR \end{array}\right. ,$$

the object being to endeavor to obtain evidence of the existence, in these compounds, of the group R_2NH. Although the behavior of hydroxylamine and phenylhydrazine towards ethyl camphoroxalate, which has already been referred to (pp. 218, 220) makes it highly probable that the amine attacks the group $>$COH, yet the possibility of the carbonyl group of the camphor nucleus first reacting with the amine must also be recognized, this, however, would involve the following changes:



$$C_8H_{14}\left\langle\begin{array}{l} C : COHCOOH \\ | \\ CO \end{array}\right. + R : NH_2 \rightarrow C_8H_{14}\left\langle\begin{array}{l} C : COHCOOH \\ | \\ C : NR \end{array}\right. ,$$

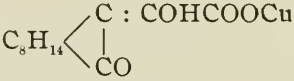
that is, the : C.OH group would remain intact and should be capable of recognition as such, but this was not found to be the case. The alternative suggestion is that intramolecular rearrangement might take place and result in the change :



At present there is no evidence in support of this latter view, while the fact that, apart from the salt forming action of the carboxyl group, camphoroxalic acid combines with amines in equimolecular proportion would appear to be decisively against it.

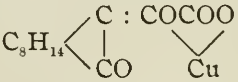
METALLIC SALTS OF CAMPHOROXALIC ACID.

When copper nitrate is allowed to react with camphoroxalic acid, in a solution of 50 per cent alcohol, at ordinary temperatures, a greenish, crystalline mass is obtained, which melts and decomposes at 275° and has the formula $C_{12}H_{14}O_4Cu$. The product is the same, irrespective of the proportions in which the copper nitrate and acid are mixed. Two views are possible of the constitution of this salt ; if the copper is present in the cuprous condition, it would be



(I.) ;

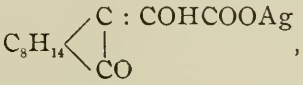
if in the cupric state, the formula



(II.),

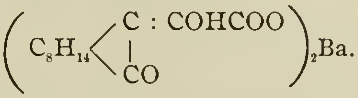
would apply and analysis could, of course, not distinguish between them. At first sight, Formula I., where the carboxyl group only is affected, would seem to be the more probable, and this view might be thought to derive support from the observation that, when the salt is heated, in alcoholic solution, at 100°, cuprous oxide is deposited. The view that the salt is represented by Formula II. is based upon the following facts : Its green color is characteristic of the cupric but not of the cuprous state. In solution the salt fails to give any indication of the presence of copper ions, which behavior is entirely in accordance with Formula II. Moreover, unlike the barium salt described below, this one gives no coloration with ferric chloride and alcohol, indicating that a change has taken place in the :COH group of the camphoroxalic acid. The decomposition, on heating at 100°, is doubtless analogous to that of Fehling's solution, in which the copper is certainly in the cupric state. According to this view, the compound is a representative of a combination of two distinct types of organo-metallic derivatives, *viz.*, the salt of a carboxylic acid and the metallic derivative of a diketone, such as the sodium derivative of ethyl acetoacetate.

When a solution of silver nitrate, in 50 per cent alcohol, is allowed to react with camphoroxalic acid, a colorless *silver salt*,



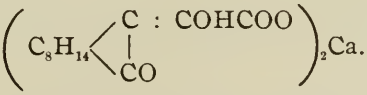
$$C_8H_{14}\left\langle\begin{array}{l} C : COHCOOAg \\ | \\ CO \end{array}\right. ,$$

is formed. Under similar conditions barium nitrate and camphoroxalic acid form a *barium salt*,



$$\left(C_8H_{14}\left\langle\begin{array}{l} C : COHCOO \\ | \\ CO \end{array}\right.\right)_2Ba.$$

Calcium nitrate reacts in the same manner, forming the *calcium salt*,



$$\left(C_8H_{14}\left\langle\begin{array}{l} C : COHCOO \\ | \\ CO \end{array}\right.\right)_2Ca.$$

In the case of ferric chloride and camphoroxalic acid, the compound which is formed has the characteristic, dark, reddish-violet color, which results, in general, when ferric chloride acts, in alcoholic solution, on a compound containing the enol grouping. This substance is somewhat similar to the compounds prepared by R. Schieff, in his work on acetoacetic ester when in combination with benzyl aniline.[1]

Its constitution seems to be represented by the formula

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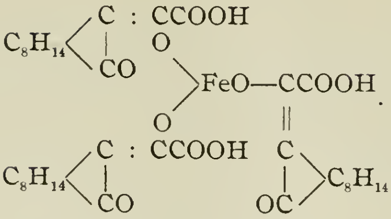
[1] Ber. d. chem. Ges., **31**, 205, 601.



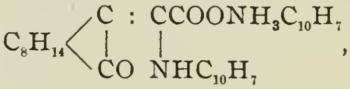
This is based on the results obtained by analysis and on the fact that the salt dissolves slowly in boiling sodium carbonate solution. It melts at about 85°.

ACTION OF AMINES ON CAMPHOROXALIC ACID.

I. β-NAPHTHYLAMINE.

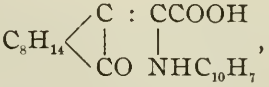
β-Naphthylamine and camphoroxalic acid yield three compounds : see errata p. 625

1. The first of these, *β-naphthylamine β-naphthylcamphoformeneaminecarboxylate,*



is formed in hot alcoholic solution and crystallizes in slender, pale-yellow needles, melting at 169°.

2. The second compound is obtained when this salt, in very dilute alcoholic solution, is treated with sodium hydroxide and the product acidified. *β-Naphthylcamphoformeneaminecarboxylic acid,*



crystallizes from alcohol in slender, bright-yellow needles, melting at 172°.5. This compound has been previously described by J. Bishop Tingle and Alfred Tingle.[1]

3. The third compound from β-naphthylamine and camphoroxalic acid, *β-naphthylcamphoformeneamine,*

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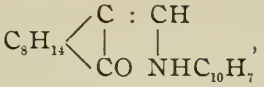
[1] J. Am. Chem. Soc., **23**, 375 (1901).

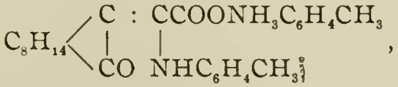


is formed by heating either of the preceding substances above its melting-point. It crystallizes in slender, pale-yellow prisms, melting at 173°.

II. PARATOLUIDINE.

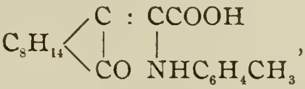
Paratoluidine and camphoroxalic acid yield a series of three compounds, corresponding to those formed by β-naphthylamine.

1. The *p-toluidine p-tolylcamphoformeneaminecarboxylate*,



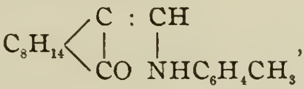
is formed in alcoholic solution and crystallizes readily from alcohol in pale-yellow needles, melting at 152°.

2. *p-Tolylcamphoformeneaminecarboxylic acid*,



is formed from the above salt by treatment with sodium hydroxide solution and subsequent acidification of the product. It crystallizes from benzene in pale-yellow prisms, melting at 168°.

3. *p-Tolylcamphoformeneamine*,

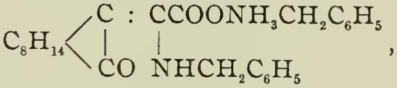


is formed by heating either of the two preceding substances above its melting-point. From alcohol it crystallizes in slender, yellow prisms, melting at 178°.

III. BENZYLAMINE.

Benzylamine forms, with camphoroxalic acid, a series of three compounds, similar to those produced by β-naphthylamine and *p*-toluidine.

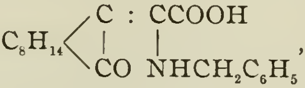
1. *Benzylamine benzylcamphoformeneaminecarboxylate,*



$$C_8H_{14}\left\langle\begin{array}{ll} C & : CCOONH_3CH_2C_6H_5 \\ | & \;\;| \\ CO & NHCH_2C_6H_5 \end{array}\right. ,$$

is obtained by the action of the free base on camphoroxalic acid and crystallizes from alcohol in irregular rhombohedra, melting at 174°.5.

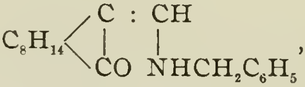
2. From the above salt free *benzylcamphoformeneaminecarboxylic acid,*



$$C_8H_{14}\left\langle\begin{array}{ll} C & : CCOOH \\ | & \;\;| \\ CO & NHCH_2C_6H_5 \end{array}\right. ,$$

is formed by treating it with sodium hydroxide and acidifying the resulting solution. It is a colorless compound, crystallizing from ethyl acetate in clusters of fine prisms, melting at 140°.

3. When heated above its melting-point, each of the preceding compounds decomposes, forming *benzylcamphoformeneamine,*

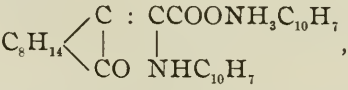


$$C_8H_{14}\left\langle\begin{array}{ll} C & : CH \\ | & \;\;| \\ CO & NHCH_2C_6H_5 \end{array}\right. ,$$

which, from alcohol, crystallizes in colorless prisms, melting at 96°.5.

IV. α-NAPHTHYLAMINE.

From α-naphthylamine and camphoroxalic acid two compounds are obtained; *α-naphthylamine naphthylcamphoformeneaminecarboxylate,*

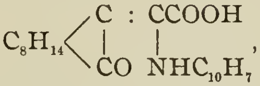


$$C_8H_{14}\left\langle\begin{array}{ll} C & : CCOONH_3C_{10}H_7 \\ | & \;\;| \\ CO & NHC_{10}H_7 \end{array}\right. ,$$

is formed in alcoholic solution and, when purified by means of this solvent, yields greenish-yellow prisms, melting at 165°.

2. The above salt, when heated with sodium hydroxide

solution and the product acidified, gives *α-naphthylcamphoformeneaminecarboxylic acid,*



$$C_8H_{14}\left\langle\begin{array}{ll} C & :\ CCOOH \\ | & \quad | \\ CO & NHC_{10}H_7 \end{array}\right. ,$$

which crystallizes from benzene with 0.5 molecule of benzene and melts at 170°.

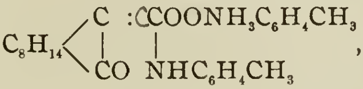
This acid has been described by J. Bishop Tingle and Alfred Tingle.[1]

3. When heated above its melting-point, each of the two preceding substances formed a viscous mass, from which no definite compound could be isolated.

V. METATOLUIDINE.

Metatoluidine and camphoroxalic acid also yield two compounds:

1. *Metatoluidine metatolylcamphoformeneaminecarboxylate,*

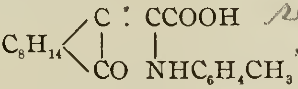


$$C_8H_{14}\left\langle\begin{array}{ll} C & :\ CCOONH_3C_6H_4CH_3 \\ | & \quad | \\ CO & NHC_6H_4CH_3 \end{array}\right. ,$$

see errata p. 625

is formed when the free acid and amine react in alcoholic solution; it crystallizes from alcohol in fine, pale lemon colored needles, melting at 126°.

2. The above salt, when treated with sodium hydroxide solution and the product acidified, gives *metatolylcamphoformeneaminecarboxylic acid,*



$$C_8H_{14}\left\langle\begin{array}{ll} C & :\ CCOOH \\ | & \quad | \\ CO & NHC_6H_4CH_3 \end{array}\right. ,$$

see errata p. 625

which crystallizes from benzene in colorless needles and melts at 154°. When heated above its melting-point, each of the preceding substances formed a viscous mass, from which no definite compound could be isolated.

VI. DIETHYLAMINE.

Diethylamine and camphoroxalic acid react, in alcoholic solution, to form two compounds:

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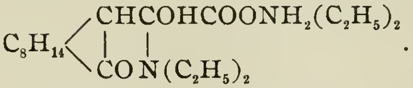
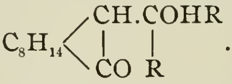
[1] J. Am. Chem. Soc., 23, 375 (1901).

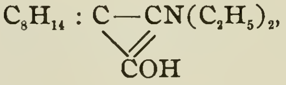
1. *Diethylamine Diethylcamphoformolaminecarboxylate,*



$$C_8H_{14}\left\langle\begin{array}{l}CHCOHCOONH_2(C_2H_5)_2\\ |\qquad |\\ CO\;N(C_2H_5)_2\end{array}\right. .$$

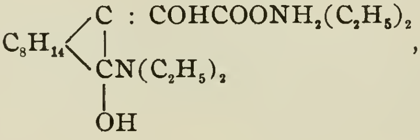
This compound crystallizes from alcohol in colorless needles, melting at 139°.5. It differs from the foregoing salts of camphoformeneaminecarboxylic acid in that its formation does not involve the elimination of the elements of water, in which respect it resembles the hydroxylamine derivative previously referred to (p. 218). With an alcoholic solution of ferric chloride no color reaction is produced. The term "*camphoformol*" is suggested for the complex  $C_8H_{14}\left\langle\begin{array}{l}CH.COHR\\ |\qquad |\\ CO\;\;R\end{array}\right.$. It differs from "*camphoformene*" by the addition of the elements of water, one hydrogen atom being united to the camphor nucleus.

2. When this salt is heated above its melting-point it gives off water, carbonic anhydride and diethylamine and forms a compound of the same empirical formula as diethyl camphoformeneamine, $C_{15}H_{25}NO$, but which differs from what we should expect of that substance by virtue of the fact that, with ferric chloride and alcohol, it gives the reddish-violet color characteristic of the enol grouping ; this seems to indicate that the reaction leading to its formation is hardly so simple as that which yields the corresponding derivatives of other amines. It may be possible that an isomeric compound,



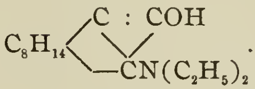
$$\begin{array}{l}C_8H_{14} : C-CN(C_2H_5)_2,\\ \qquad\qquad \diagdown\!\!/\!\!/\\ \qquad\qquad COH\end{array}$$

is produced, or it may be that diethylamine and camphoroxalic acid yield, first, the hypothetical compound,



$$C_8H_{14}\left\langle\begin{array}{l}C : COHCOONH_2(C_2H_5)_2\\ |\\ CN(C_2H_5)_2\\ |\\ OH\end{array}\right. ,$$

which, when heated, would doubtless give a body with the formula

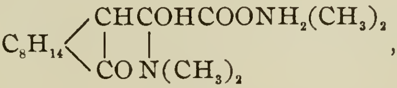


This matter will be investigated at the first suitable opportunity, because the substance in question might furnish an interesting case of dynamic isomerism.

The compound crystallizes from ethyl acetate in colorless needles, melting at 153°.

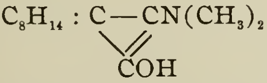
VII. DIMETHYLAMINE.

1. Dimethylamine and camphoroxalic acid, in alcoholic solution, react to form *dimethylamine dimethylcamphoformolaminecarboxylate*,

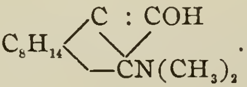


which crystallizes from acetone in colorless needles, melting at 137°.5. Like the corresponding compound from diethylamine it is, apparently, formed by the direct combination of acid and base, without the loss of a molecule of water.

2. When the salt which has just been described is heated above the melting-point, it decomposes, similarly to the analogous diethyl compound and forms a substance of the same empirical formula as dimethylcamphoformeneamine, $C_{13}H_{21}NO$, but which, on account of the fact that it gives a color reaction with ferric chloride, does not seem to have that structure. It appears probable that its constitution is similar to that of the diethyl derivative and that its formula is,



or



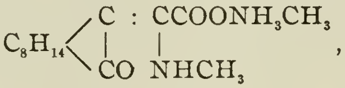
It crystallizes from alcohol in colorless needles, melting at 63°.

It is worthy of note that dimethylamine and diethylamine are the only two secondary amines from which it has been possible to obtain derivatives with camphoroxalic acid. Methylaniline and ethylaniline entirely fail to give definite compounds under similar conditions; whether this is due to the general tendency of these two substances to yield oily salts, or to their feebler basic properties as compared with the aliphatic amines or to some other cause must, at present, remain uncertain.

VIII. METHYLAMINE.

Methylamine forms two compounds with camphoroxalic acid:

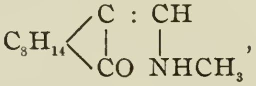
1. *Methylamine methylcamphoformeneaminecarboxylate,*



$$C_8H_{14}\left\langle\begin{array}{ll} C & : CCOONH_3CH_3 \\ | & \quad | \\ CO & \ NHCH_3 \end{array}\right. ,$$

which crystallizes from alcohol in slender, colorless needles, melting at 172°.

When this salt is heated above its melting-point, it forms *methylcamphoformeneamine,*

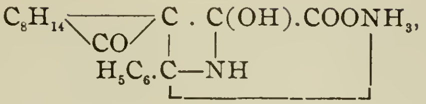


$$C_8H_{14}\left\langle\begin{array}{ll} C & : CH \\ | & \quad | \\ CO & \ NHCH_3 \end{array}\right. ,$$

which crystallizes from ethyl acetate in colorless needles, melting at 131°.

IX. BENZAMIDINE.

Camphoroxalic acid, in alcoholic solution, reacts with benzamidine, in equimolecular proportion, to form a colorless, crystalline compound, melting at 184°. At a slightly higher temperature it decomposes to a carbonaceous mass. Dilute acids and solutions of alkalies seem to have no effect upon the compound and ferric chloride, in alcoholic solution, does not give any color reaction. The substance has the empirical formula $C_{19}H_{24}O_4N_2$. Its constitution may, perhaps, be represented by the expression

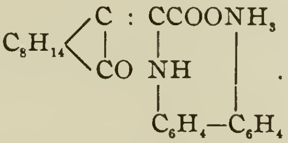


$$C_8H_{14}\langle CO \rangle C\,.\,C(OH).COONH_3, \quad H_5C_6.C—NH$$

but further work will be necessary to decide this point.

X. BENZIDINE.

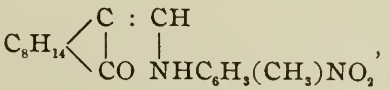
Benzidine reacts with camphoroxalic acid, in hot alcoholic solution, eliminating water and forming a greenish-yellow, crystalline mass, which melts at 190° and decomposes, when maintained at this temperature or heated for a short time at a higher one. The compound is, apparently, unchanged by the action of acids or alkalies and does not give any coloration with ferric chloride, in alcoholic solution. In view of these facts and of the properties of benzidine itself, it is probable that one of the amino groups has combined with the :COH group with the elimination of water, while the other has reacted with the carboxyl hydrogen to form a salt, as represented by the formula



$$C_8H_{14}\begin{cases} C : CCOONH_3 \\ CO \quad NH \end{cases} \quad C_6H_4—C_6H_4 .$$

XI. 1,2,4-NITROTOLUIDINE.

When nitrotoluidine ($CH_3 = 1$; $NH_2 = 2$; $NO_2 = 4$) is heated, at 150°, with camphoroxalic acid, in alcoholic solution, under pressure, for several hours, *nitrotolylcamphoformeneamine,*

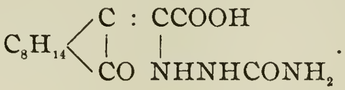


$$C_8H_{14}\begin{cases} C : CH \\ CO \quad NHC_6H_3(CH_3)NO_2 \end{cases},$$

is obtained. It crystallizes readily from alcohol in minute, bright yellow needles, which melt at 192°. It was not possible to isolate the corresponding carboxylic acid or salt, although a number of experiments, under varying conditions, were made with this object.

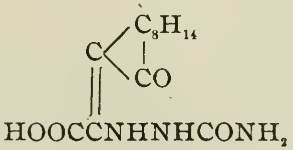
XII. SEMICARBAZINE.

When semicarbazine and camphoroxalic acid react in the presence of acetic acid, a compound is formed with the composition of *semicarbazine camphoformeneaminecarboxylic acid*,



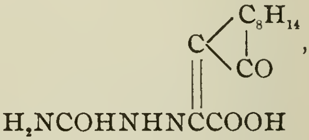
$$C_8H_{14}\left\langle\begin{array}{lll} C & : & CCOOH \\ | & & | \\ CO & & NHNHCONH_2 \end{array}\right. .$$

It crystallizes from alcohol in stout, colorless prisms, melting at 200°. When dissolved in boiling glacial acetic acid, crystals were deposited in the form of clusters of fine needles, which melt at 209°–210°. If the compound obtained from glacial acetic acid is dissolved in sodium carbonate and reprecipitated by acid, a gelatinous substance is formed which crystallizes from acetone in slender, colorless needles, melting at the same temperature as before, *viz.*, 209°–210°. These two substances have the same empirical formula and maintain their distinctive melting-points, even after heating for some time at 110°. They dissolve readily in sodium hydrogen carbonate and are reprecipitated by acids in the form of a jelly. With alcoholic ferric chloride, no color reaction is produced in either case. All these facts lead to one of two conclusions: either the compounds are stereoisomers of the maleic-fumaric type,



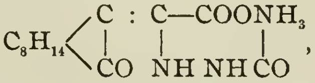
$$\begin{array}{l} C\left\langle\begin{array}{l} C_8H_{14} \\ | \\ CO \end{array}\right. \\ \| \\ HOOCCNHNHCONH_2 \end{array}$$

and



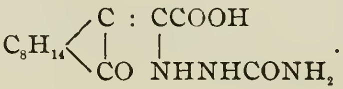
$$\begin{array}{r} C\left\langle\begin{array}{l} C_8H_{14} \\ | \\ CO \end{array}\right. , \\ \| \quad\quad\quad \\ H_2NCOHNHNCCOOH \end{array}$$

or there is the formation of an inner salt,



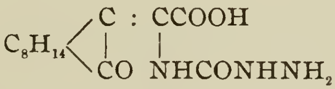
$$C_8H_{14}\left\langle\begin{array}{llll} C & : & C\text{—}COONH_3 & \\ | & & | & | \\ CO & & NH\ NH & CO \end{array}\right. ,$$

which is changed by the glacial acetic acid into the open-chain compound,



$$C_8H_{14}\left\langle\begin{array}{lll} C & : & CCOOH \\ | & & | \\ CO & & NHNHCONH_2 \end{array}\right. .$$

In the case of these semicarbazine derivatives we have represented the condensation as having taken place between the hydrazine nucleus and the camphoroxalic acid. Although this is in accordance with precedent, it may well be that in one or both compounds it is the carbamide group which has reacted, giving



$$C_8H_{14}\left\langle\begin{array}{l}C : CCOOH \\ \mid \qquad \mid \\ CO \quad NHCONHNH_2\end{array}\right.$$

and its stereoisomer. Further work will be necessary to decide between these various possibilities; the subject is being more fully investigated in this laboratory.

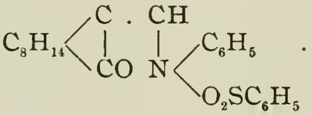
XIII. ORTHOPHENYLENEDIAMINE.

When orthophenylenediamine and camphoroxalic acid are allowed to react in alcoholic solution, at the ordinary temperature, there is formed the camphoquinoxaline compound, which was prepared by J. Bishop Tingle by the action of sodium camphoroxalate and also of ethyl camphoroxalate on orthophenylenediamine. It crystallizes from alcohol in bright yellow needles, which melt at 246°. The formation of this camphoquinoxaline, by the interaction of sodium camphoroxalate, ethyl camphoroxalate or camphoroxalic acid, respectively, is somewhat remarkable, as it shows the tendency of such a phenylene diamine derivative, in which the amino groups are in the ortho position, to form a five-membered ring compound, even under conditions where we should not expect such an action to take place.

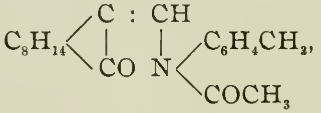
PARAPHENYLENEDIAMINE was treated with camphoroxalic acid under the same conditions as were used for the ortho-compound and also under others, in the hope that it might react and throw some light on this question of ring formation, but no definite product could be obtained.

ACTION OF ACYLATING AGENTS ON CAMPHOFORMENE DERIVATIVES.

The condensation compounds from primary amines, described in the preceding pages and those previously prepared by Bishop Tingle, are represented as containing an imino group. This view of their constitution was based on the nature of the compounds formed from hydroxylamine and phenylhydrazine. It is very desirable to obtain some direct evidence on this point and, consequently, the study of acylating agents on camphoformene derivatives was commenced. Bishop Tingle had previously shown that, with phenylsulphonic chloride, by the Schotten-Baumann reaction, phenylcamphoformeneamine forms a compound which crystallizes from benzene in colorless needles and melts at 133°, but its composition was not determined. This work was repeated and a similar compound was obtained, it melted at 133° and, on standing in the air, soon began to decompose. It was found to be the *phenylcamphoformeneaminephenylsulphone*,



Acetyl chloride, when allowed to react with *p*-tolylcamphoformeneamine, replaces the iminic hydrogen and forms *acetyl p-tolylcamphoformeneamine*,



which is a colorless, crystalline compound, melting at 161°. The reaction of these two chlorides with the above typical camphoformeneamines, resulting in the elimination of hydrochloric acid and the formation of the sulphone and acetyl derivatives, seems to be rather conclusive evidence in favor of the structure which has been suggested for the camphoformeneamines and, as we know that these bodies are formed from the corresponding carboxylic acids by the elimination fo carbonic anhydride, the formulæ assigned to these acids also seem to be confirmed.

Chloracetyl chloride, when allowed to react with β-naphthylcamphoformeneamine, yields a colorless, crystalline compound, melting at 63° ; unfortunately, on account of its instability, it could not be analyzed.

The following table (pp. 236–237) shows the various condensation compounds of camphoroxalic acid and amines which have hitherto been prepared. They are arranged in type classes and their melting-points are given. The compounds marked * have been previously described by J. Bishop Tingle and Alfred Tingle.[1] Those marked + contain the elements of 1 molecule of water more than is shown in the type formula. Their constitution has been discussed on p. 228 *et seq.* In cases where no definite compound could be isolated, the space in the table is occupied by a dash.

EXPERIMENTAL.

Camphoroxalic acid was prepared according to the method worked out by J. Bishop Tingle[2] as follows:

Camphor (31.5 grams) and ethyl oxalate (22 grams) were dissolved in 400 cc. of anhydrous petroleum ether, of 85°–100° boiling-point and 3.5 grams of sodium wire were added. The mixture was boiled on a water-bath, with a reflux condenser, until the violent action had ceased and the sodium had almost entirely dissolved; it was then allowed to remain over night, at the ordinary temperature, protected from moisture. The solution, after standing, was well shaken with about an equal volume of ice-water and the petroleum ether extract separated from the water and dried over calcium chloride. The dried liquid was distilled, at first from the water-bath; when the temperature of the boiling liquid rises to almost 90°, the pressure is somewhat reduced and the distillation continued, care being taken not to allow the temperature of the liquid in the flask to rise above 130°; frequently it is unnecessary to heat above 120°–125°.

The aqueous solution was then well cooled and acidified with dilute sulphuric acid, then extracted three or four times with ether, until a portion of the fresh ether extract showed only a pale reddish-violet color with alcohol and ferric chloride. The ether was dried over calcium chloride and, after filtering, was distilled off and the residue added to that

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[1] J. Am. Chem. Soc., **23**, 364 (1901).

[2] *Ibid.*, **23**, 364 (1901).

Table I.

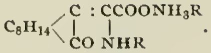
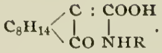
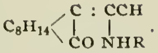
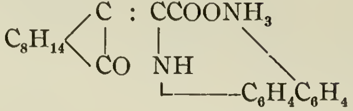
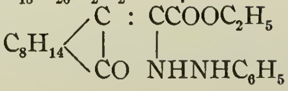
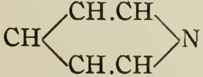
Amines.	 $C_8H_{14}\left\langle\begin{matrix}C & : & CCOONH_3R\\ \vert & & \vert\\ CO & & NHR\end{matrix}\right.$.	 $C_8H_{14}\left\langle\begin{matrix}C & : & COOH\\ \vert & & \vert\\ CO & & NHR\end{matrix}\right.$.	 $C_8H_{14}\left\langle\begin{matrix}C & : & CCH\\ \vert & & \vert\\ CO & & NHR\end{matrix}\right.$.	
I. $C_{10}H_7.NH_2$ β	169°	*m. p. 172°.5	173°	
II. $C_6H_4.CH_3.NH_2$ [1 : 4]	152°	168°	178°	
III. $C_6H_5.CH_2.NH_2$	147°.5	140°	96°.5	
IV. $C_{10}H_7.NH_2$ α	165°	*170°	———	
V. $CH_3C_6H_4NH_2$ [1 : 3]	126°	154°	———	
VI. $NH(C_2H_5)_2$	+139°.5	———	153°	
VII. $NH(CH_3)_2$	+137°.5	———	63°	
VIII. NH_2CH_3	172°	———	131°	
IX. $C_6H_5C(NH_2) : NH$	———	———	———	$C_{19}H_{24}N_2O_4$. 184°
X. $NH_2C_6H_4.C_6H_4NH_2$	———	———	———	 190°
XI. $\overset{1}{C}H_3C_6H_3\overset{2}{N}H_2.\overset{4}{N}O_2$	———	———	192°	
XII. $NH_2CONHNH_2$	200° and 209°–210°	———	———	
XIII. $C_6H_5NH_2$	*158°	*174°	*166°	
XIV. NH_2OH	———	*+146°.5	———	
XV. NH_3	———	*178°	———	
XVI. $C_6H_4(NH_2)_2$ [1 : 2]	———	———	———	+$C_{18}H_{20}N_2O_2$ 246°
XVII. $NH_2NHC_0H_5$	———	———	———	+  212°

Table I. (Continued).

Amines.	$C_8H_{14}\begin{matrix} C : CCOONH_3R \\ \vert \quad \vert \\ CO \quad NHR \end{matrix}$.	$C_8H_{14}\begin{matrix} C : CCOOH \\ \vert \quad \vert \\ CO \quad NHR \end{matrix}$.	$C_8H_{14}\begin{matrix} C : CH \\ \vert \quad \vert \\ CO \quad NHR \end{matrix}$.
XVIII. $CH_3CONHNHC_6H_5$	—	—	—
XIX. $OC(NH_2)_2$	—	—	—
XX. $NH_2C_6H_4NO_2$ [1 : 4]	—	—	—
XXI. $CH_3COC_6H_4NH_2$ [1 : 4]	—	—	—
XXII. $C_6H_5NHCH_3$	—	—	—
XXIII. $C_6H_5NHC_2H_5$	—	—	—
XXIV. $C_6H_5NHCH_2C_6H_5$	—	—	—
XXV. $C_2H_4(NH_2)_2$	—	—	—
XXVI. $C_6H_5NHNHCH_2C_6H_5$	—	—	—
XXVII. $(NH_2)_2C : NH$	—	—	—
XXVIII.  $CH\begin{matrix} CH.CH \\ CH.CH \end{matrix}N$	—	—	—
XXIX. $C_6H_5N(CH_3)_2$	—	—	—
XXX. $CH_3C_6H_4NH_2$ [1 : 2]	—	—	—
XXXI. $NH_2NHC_6H_4Br$ [1 : 4]	—	—	—
XXXII. NH_2NH_2	—	—	—

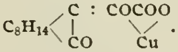
from the petroleum ether extract. This residue was extracted, several times, by boiling with a 10 per cent solution of potassium hydroxide, until the filtrate, after acidification, no longer gave a marked color with alcohol and ferric chloride. The alkaline solution, from the filtered extracts, was then acidified with dilute sulphuric acid and, after standing several hours, the crystalline precipitate was filtered off. This crystalline mass was purified by recrystallization from petroleum ether, by means of a Soxhlet apparatus. The mother-liquors from the recrystallizations and the residue in the Soxhlet apparatus were treated with sodium carbonate, the solution filtered, acidified and the resulting precipitate recrystallized.

CAMPHOROXALIC ACID DERIVATIVES.

METALLIC SALTS OF CAMPHOROXALIC ACID.

Copper Camphoroxalate.—The acid (1 molecule) and copper nitrate (0.5 molecule) were separately dissolved in 50 per cent alcohol, the solutions mixed and allowed to evaporate at the ordinary temperature. Although the pure and dry copper salt does not melt below 275°, it was found that, if the solution was heated on a water-bath, to remove the excess of alcohol, the green salt formed, with part of the solvent, an oily layer which was extremely difficult to purify. When it is allowed to crystallize at the ordinary temperature, it is deposited as a fine, green, crystalline powder, which melts and decomposes at 275°. With ferric chloride, in alcoholic solution, this salt gives no coloration. If an alcoholic solution of the salt is heated for some time at 100°, it undergoes decomposition and deposits cuprous oxide. Analysis :

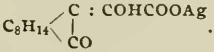
2.1686 grams salt gave 0.0474 gram CuO.

	Calculated for  $\mathrm{C_8H_{14}}\left\langle\begin{array}{l}\mathrm{C : COCOO}\\ \mid \qquad\quad \diagdown\diagup \\ \mathrm{CO}\qquad\quad \mathrm{Cu}\end{array}\right.$.	Found.
Cu	22.28	22.46

The proportion of the reacting substances was varied, in the hope that another salt, of different composition, might be formed, but, in all cases, the resulting compound was identical with the one described above.

2. *Silver Camphoroxalate.*—Silver nitrate and camphoroxalic acid were allowed to react in a solution of 50 per cent alcohol and, on allowing the solvent to evaporate spontaneously, a colorless, crystalline mass was obtained, which was purified by repeated recrystallization from alcohol. The resulting compound was found to melt and decompose at 137°. Analysis:

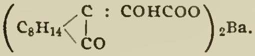
0.2975 gram salt gave 0.0965 gram Ag.

	Calculated for  $C_8H_{14}<\begin{array}{l}C : COHCOOAg\\ \vert\\ CO\end{array}.$	Found.
Ag	32.63	32.47

As in the preparation of the copper salt, different proportions of silver nitrate and camphoroxalic acid were allowed to react but, in this case also, only one compound could be isolated.

3. *Barium Camphoroxalate.*—Barium nitrate (1 molecule) and camphoroxalic acid (2 molecules), in a solution of 50 per cent alcohol, were allowed to evaporate. These deposited a colorless, crystalline compound, which was recrystallized from alcohol. With ferric chloride and alcohol a reddish-violet color, characteristic of the presence of the enol grouping, was produced. Analysis:

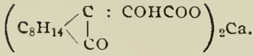
0.1728 gram salt gave 0.0682 gram $BaSO_4$.

	Calculated for  $\left(C_8H_{14}<\begin{array}{l}C : COHCOO\\ \vert\\ CO\end{array}\right)_2Ba.$	Found.
Ba	23.56	23.21

The proportions of the reacting substances were varied, as in the preceding cases, but no other salt could be obtained.

4. *Calcium Camphoroxalate.*—Calcium nitrate (1 molecule) and camphoroxalic acid (2 molecules) were mixed in solution of 50 per cent alcohol, under the same conditions as in the case of the barium salt; on evaporation and recrystallization from alcohol, colorless crystals were deposited. Analysis:

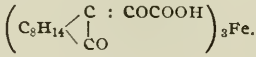
0.2067 gram salt gave 0.0537 gram $CaSO_4$.

	Calculated for  $\left(C_8H_{14}\left\langle\begin{matrix}C : COHCOO\\ \vert \\ CO\end{matrix}\right.\right)_2Ca.$	Found.
Ca	8.22	8.4

In the case of the calcium salt also, only one compound could be obtained.

5. *Ferric Camphoroxalate.*—Ferric chloride (1 molecule) and camphoroxalic acid (2 molecules) were mixed in solution of 50 per cent alcohol. A deep, reddish-violet coloration was produced but from no solvent could a crystalline compound be obtained and the viscous substance, deposited by the evaporation of the original liquid to dryness, gave percentages of iron which showed that it had no definite composition, hence the following method was employed: The alcoholic solution of the reaction-product, formed by the camphoroxalic acid and ferric chloride, was diluted with water in order to precipitate any unchanged camphoroxalic acid and, at the same time, to dissolve the dark-red substance in solution in the alcohol. After filtering, ether was added to the liquid, but, on account of the presence of free hydrochloric acid which had been formed by the reaction of the camphoroxalic acid and ferric chloride, the ether dissolved and formed a homogenous solution with the original liquid. When this mixed ethereal-aqueous liquid was saturated with sodium chloride the ether took up the red compound and separated from the aqueous layer; this latter was removed and the ethereal solution dried over calcium chloride. The ether was then evaporated from the water-bath. A glassy, almost black mass remained. It is soluble, to a slight extent, in boiling sodium carbonate solution. The compound should, probably, be regarded as being camphoroxalic acid in which the hydrogen atom of the enol group :COH has been replaced by iron, while the carboxyl group remained intact on account of the presence of hydrochloric acid in the liquid during the reaction. Analysis:

0.2095 gram substance gave 0.0235 gram Fe_2O_3.

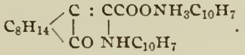
	Calculated for  $\left(C_8H_{14}\left\langle\begin{matrix}C : COCOOH\\ \vert \\ CO\end{matrix}\right.\right)_3Fe.$	Found.
Fe	7.72	7.8

AMINE DERIVATIVES OF CAMPHOROXALIC ACID.

I. β-NAPHTHYLAMINE.

1. β-Naphthylamine (6.4 grams = 2 molecules) and camphoroxalic acid (5 grams = 1 molecule) were mixed in boiling alcoholic solution, which was then kept at about 100°, on a water-bath, for a few minutes. Fine, yellow needles soon began to separate out and, on cooling, a mass of such crystals was deposited. The yield was almost quantitative. The compound is fairly readily soluble in hot alcohol and is purified by recrystallization from it. The purified compound was deposited in the form of fine needles, of a pale yellow color and melted at 169°, with the evolution of a gas. Analysis showed it to be *β-naphthylamine β-naphthylcamphoformeneaminecarboxylate.*

0.1723 gram substance gave 8.6 cc. N at 18° and 770 mm.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}C : CCOONH_3C_{10}H_7\\ \vert \quad \vert\\ CO\ NHC_{10}H_7\end{array}\right.$.	Found.
N	5.66	5.74

This salt when treated, in alcoholic solution, with ferric chloride, did not give the violet-red color characteristic of the enol grouping.

2. When the above compound is heated with a solution of sodium hydroxide, it dissolves, forming sodium β-naphthylcamphoformeneaminecarboxylate and liberating β-naphthylamine, which is deposited, on cooling the liquid and was identified by its melting-point, 112°. On acidification of the solution of the sodium salt with dilute hydrochloric acid, the free β-naphthylcamphoformeneaminecarboxylic acid is precipitated. It was purified by recrystallization from benzene and is deposited in yellow needles, melting at 172°.5–173°. This corresponds to the melting-point obtained for the same compound which was prepared by J. Bishop Tingle.[1] The acid dissolves readily in sodium carbonate solution with the evolution of carbonic anhydride and, in alcoholic solution, produces no red color with ferric chloride.

3. When β-naphthylamine β-naphthylcamphoformeneamine-

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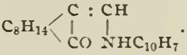
[1] J. Am. Chem. Soc., **23**, 375 (1901).

carboxylate is heated above its melting-point, it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate, when it was led into a solution of barium hydroxide. A white solid sublimes into the upper part of the tube in which the fusion is being made and, by its melting-point, was shown to be β-naphthylamine. The fused material, after the evolution of gas had ceased, is purified by means of alcohol and crystallizes in pale yellow needles, melting at 173°. Analysis showed it to be *β-naphthylcamphoformeneamine.*

0.1783 gram substance gave 7.1 cc. N at 12° and 760 mm.

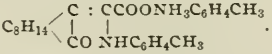
	Calculated for  $C_8H_{14}\left\langle\begin{array}{ll} C & : CH \\ \vert & \quad \vert \\ CO & NHC_{10}H_7 \end{array}\right.$.	Found.
N	4.59	4.73

With ferric chloride, in alcoholic solution, no violet-red color was produced. When β-naphthylcamphoformeneamine-carboxylic acid is heated above its melting-point it gives off carbonic anhydride and forms a compound, melting at 173°, identical with that formed from the β-naphthylamine β-naphthylcamphoformeneaminecarboxylate by heating.

II. PARATOLUIDINE.

Camphoroxalic acid (5 grams = 1 molecule) and paratoluidine (4.8 grams = 2 molecules) were mixed in boiling alcoholic solution, which, on cooling, deposited a mass of fine yellow needles. The yield seemed to be nearly quantitative. The compound is soluble in alcohol and is purified by recrystallization from it. The purified compound crystallizes in slender, yellow needles and melts at 152°, with the evolution of a gas. With ferric chloride, in alcoholic solution, it gave no color reaction. Analysis proved it to be *paratoluidine paratolylcamphoformeneaminecarboxylate.*

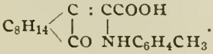
0.1818 gram substance gave 10.2 cc. N at 13° and 765 mm.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{ll} C & : CCOONH_3C_6H_4CH_3 \\ \vert & \quad \vert \\ CO & NHC_6H_4CH_3 \end{array}\right.$.	Found.
N	6.66	6.67

2. When the above compound is heated with sodium hy-

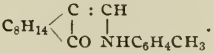
droxide solution, it dissolves, forming *sodium paratolylcamphoformeneaminecarboxylate* which, on acidification with dilute hydrochloric acid, precipitates the free *paratolylcamphoformeneaminecarboxylic acid;* this is insoluble in water and forms a pale yellow mass. The substance, after recrystallization from benzene, is deposited in yellow needles and melts at 168°, with the evolution of a gas. It dissolves in sodium carbonate solution with the liberation of carbonic anhydride and, with an alcoholic solution of ferric chloride, produces no color. Analysis showed it to be *paratolylcamphoformeneaminecarboxylic acid.*

0.1605 gram substance gave 6.2 cc. N at 6° and 770 mm.

	Calculated for  $C_8H_{14}<\begin{matrix}C & : & CCOOH\\ \vert & & \vert\\ CO & & NHC_6H_4CH_3\end{matrix}.$	Found.
N	4.47	4.64

3. When the paratoluidine paratolylcamphoformeneaminecarboxylate is heated above its melting-point it gives off a gas which was proved to be carbonic anhydride by the production of barium carbonate, when it was led into a solution of barium hydroxide. When the tube in which the fusion is being made is allowed to cool, a white, crystalline solid appears in its upper part; this, by its melting-point, 42°.5, was demonstrated to be paratoluidine. The fused material, after the evolution of gas had ceased, was recrystallized from alcohol and is deposited in very pale yellow crystals, melting at 178°. With alcoholic ferric chloride no color is produced. Analysis showed it to be *paratolylcamphoformeneamine.*

0.1710 gram substance gave 7.8 cc. N at 12° and 755 mm.

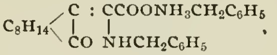
	Calculated for  $C_8H_{14}<\begin{matrix}C & : & CH\\ \vert & & \vert\\ CO & & NHC_6H_4CH_3\end{matrix}.$	Found.
N	5.20	5.37

When paratolylcamphoformeneaminecarboxylic acid is heated above its melting-point it gives off carbonic anhydride and forms a compound, melting at 178°, identical with the one just described, which is formed by heating the paratoluidine salt of this acid.

III. BENZYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and benzylamine (4.6 grams = 2 molecules) were mixed in hot alcoholic solution and, after evaporating off part of the solvent on the water-bath and cooling, a colorless, crystalline mass was gradually deposited. After recrystallization from alcohol it was obtained in the form of distorted rhombohedra, melting at 147°.5 with the evolution of a gas. With alcoholic ferric chloride no color was produced. Analysis showed it to be *benzylamine benzylcamphoformeneaminecarboxylate.*

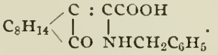
0.2251 gram substance gave 15.7 cc. N at 18° and 770 mm.



	Calculated for $C_8H_{14}\left\langle\begin{array}{ll}C & :CCOONH_3CH_2C_6H_5\\ \vert & \vert\\ CO & NHCH_2C_6H_5\end{array}\right.$,	Found.
N	7.95	8.16

2. When the above compound is heated with sodium hydroxide solution it dissolves, forming sodium benzylcamphoformeneaminecarboxylate. The addition of dilute hydrochloric acid, in excess, to this solution produces a gummy precipitate, which solidifies after standing in contact with water and, on recrystallization from ethyl acetate, forms colorless crystals, melting at 140°. In sodium carbonate solution it dissolves with the evolution of carbonic anhydride and, with alcoholic ferric chloride, produces no color. Analysis proves it to be *benzylcamphoformeneaminecarboxylic acid.*

0.2035 gram substance gave 0.5396 gram CO_2 and 0.1395 gram H_2O.

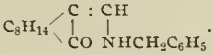


	Calculated for $C_8H_{14}\left\langle\begin{array}{ll}C & :CCOOH\\ \vert & \vert\\ CO & NHCH_2C_6H_5\end{array}\right.$.	Found.
C	72.52	72.35
H	7.35	7.6

3. Heated above its melting-point, benzylamine benzylcamphoformeneaminecarboxylate gives off a gas which proved to be carbonic anhydride by the production of barium carbonate, when it was passed into a solution of barium hydroxide. The fused material, after the evolution of gas had

ceased, was recrystallized from ethyl acetate and is deposited in colorless prisms, melting at 96°.5. With alcoholic ferric chloride no color is produced. Analysis showed it to be *benzylcamphoformeneamine.*

0.1885 gram substance gave 9.8 cc. N at 16° and 762 mm.

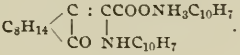
	Calculated for  $C_8H_{14}\left\langle\begin{array}{l} C : CH \\ \vert \quad\ \vert \\ CO\ \ NHCH_2C_6H_5 \end{array}\right.$.	Found.
N	6.07	5.45

If benzylcamphoformeneaminecarboxylic acid is heated above its melting-point it also gives off carbonic anhydride and forms a compound, melting at 96°.5, identical with that formed by heating the benzylamine salt of the acid.

IV. α-NAPHTHYLAMINE.

Camphoroxalic acid (5 grams = 1 molecule) and α-naphthylamine (6.4 grams = 2 molecules) were mixed in alcoholic solution. On evaporating the solvent, greenish-yellow crystals were found which, after purification from alcohol, melt at 165°, with the evolution of gas. With ferric chloride, in alcoholic solution, no color is produced. Analysis proved it to be *α-naphthylamine α-naphthylcamphoformeneaminecarboxylate.*

0.1532 gram substance gave 7.5 cc. N at 16° and 766 mm.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l} C : CCOONH_3C_{10}H_7 \\ \vert \quad\ \vert \\ CO\ \ NHC_{10}H_7 \end{array}\right.$.	Found.
N	5.66	5.75

The above salt dissolves when treated with sodium hydroxide solution, forming *sodium α-naphthylcamphoformeneaminecarboxylate*, which, on acidification with dilute hydrochloric acid, forms a yellow precipitate ; this, after crystallization from benzene, melts at 170° and is found to be identical with the same compound prepared in another way by Bishop Tingle. It dissolves in sodium carbonate with the evolution of carbonic anhydride and, with alcoholic ferric chloride, produces no color.

3. When either of the above α-naphthylamine compounds

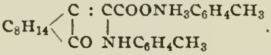
was heated, in order to obtain a camphoformeneamine derivative, a gummy substance was obtained, which could not be induced to crystallize from any solvent.

V. METATOLUIDINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and metatoluidine (4.8 grams = 2 molecules) were allowed to react in alcoholic solution ; after evaporation there were deposited fine needles of a pale lemon color which, when recrystallized from alcohol, melted at 126°. With alcoholic ferric chloride no color was produced. Analysis showed this substance to be *metatoluidine metatolylcamphoformeneaminecarboxylate.*

0.3153 gram substance gave 19 cc. N at 25° and 765 mm.

Calculated for



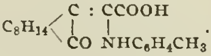
$$C_8H_{14}\left\langle\begin{array}{l} C : CCOONH_3C_6H_4CH_3 \\ \,|\qquad | \\ CO\ \ NHC_6H_4CH_3 \end{array}\right. .$$

	Calculated for	Found.
N	6.66	6.78

2. The above salt, when treated with a solution of sodium hydroxide, dissolves, forming *sodium metatolylcamphoformeneaminecarboxylate*, which, on acidification with dilute hydrochloric acid, gives a yellow precipitate. After purification from benzene, crystals are deposited melting at 154°. They dissolve in sodium carbonate solution with the evolution of carbonic anhydride and, with alcoholic ferric chloride, give no color. Analysis shows it to be *metatolylcamphoformeneaminecarboxylic acid.*

0.1497 gram substance gave 5.65 cc. N at 10° and 770 mm.

Calculated for



$$C_8H_{14}\left\langle\begin{array}{l} C : CCOOH \\ \,|\qquad | \\ CO\ \ NHC_6H_4CH_3 \end{array}\right. .$$

	Calculated for	Found.
N	4.47	4.58

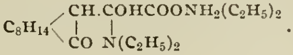
3. Both metatolylcamphoformeneaminecarboxylic acid and its metatoluidine salt, on heating, gave a gum, which could not be obtained pure enough for analysis.

VI. DIETHYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) was allowed to react with an alcoholic solution (3.4 grams = 2 molecules)

of diethylamine ; a compound crystallizing in colorless needles was obtained which, when purified by recrystallization from alcohol, melts at 139°.5 with the evolution of a gas. With alcoholic ferric chloride it gives no color reaction. By analysis the compound is shown to be *diethylamine diethylcamphoformolaminecarboxylate.*

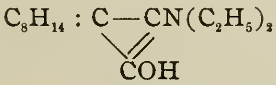
0.1983 gram substance gives 13.4 cc. N at 21° and 769 mm.

	Calculated for  $C_8H_{14}\left<\begin{array}{l}CH.COHCOONH_2(C_2H_5)_2\\ \vert \quad \vert \\ CO\ N(C_2H_5)_2\end{array}\right.$.	Found.
N	7.55	7.80

The diethylamine solution used in the preparation of this compound was prepared by dissolving diethylamine hydrochloride in absolute alcohol, adding the required amount of potassium hydroxide and filtering off the insoluble potassium chloride.

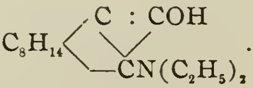
2. When treated with sodium hydroxide solution the carboxylate just described dissolves but, on acidification with dilute hydrochloric acid, it is decomposed into camphoroxalic acid and diethylamine. No method of treatment could be devised by which free diethylcamphoformolaminecarboxylic acid could be obtained.

3. When diethylamine diethylcamphoformolaminecarboxylate is heated above its melting-point, diethylamine, water and carbonic anhydride are given off and, after purification of the fused material, by crystallization from acetone, the product melts at 153°. With alcoholic ferric chloride the reddish-violet color is produced, which is so characteristic of the enol grouping. By analysis it is found to have an empirical formula identical with that of diethylcamphoformeneamine, but, on account of its behavior towards ferric chloride, its constitution seems, as previously explained (p. 228), to be represented by the formula



$C_8H_{14} : C—CN(C_2H_5)_2$, with C and $CN(C_2H_5)_2$ joined below to COH

or



$C_8H_{14}\left<\begin{array}{l}C : COH\\ —CN(C_2H_5)_2\end{array}\right.$.

Analysis:

0.2045 gram substance gave 8.1 cc. N at 16° and 762 mm.

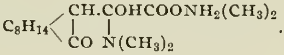
	Calculated for $C_{15}H_{25}ON$.	Found.
N	4.56	4.68

VII. DIMETHYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and dimethylamine (2 grams = 2 molecules) were allowed to react in alcoholic solution and, after part of the solvent had evaporated spontaneously, a crystalline compound was obtained. After recrystallization from acetone, colorless needles were deposited, melting at 137°.5 with the evolution of a gas. With alcoholic ferric chloride it produced no color reaction. Analysis showed it to be *dimethylamine dimethylcamphoformolamine-carboxylate.* Analysis:

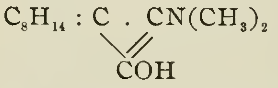
I. 0.2000 gram substance gave 0.4452 gram CO_2 and 0.1661 gram H_2O.

II. 0.2135 gram substance gave 0.4818 gram CO_2 and 0.1770 gram H_2O.

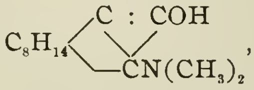
	Calculated for  $C_8H_{14}\left\langle\begin{array}{l}CH.COHCOONH_2(CH_3)_2\\ \vert \quad\ \ \vert\\ CO\ \ N(CH_3)_2\end{array}\right.$	Found. I.	Found. II.
C	61.14	60.71	61.58
H	9.55	9.29	9.27

2. When dimethylamine dimethylcamphoformolaminecarboxylate is treated with sodium hydroxide solution it dissolves but, on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and dimethylamine.

3. When heated to 140°, dimethylamine dimethylcamphoformolaminecarboxylate gives off water, carbonic anhydride and dimethylamine and forms a compound which, when purified by recrystallization from acetone, melts at 63°. With alcoholic ferric chloride it gives a purple color. The alternative formulæ,



and



for this compound are discussed on p. 228. Analysis:

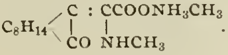
0.2458 gram substance gave 14.8 cc. N at 19° and 770 mm.

	Calculated for $C_{13}H_{21}ON$.	Found.
N	6.77	7.01

VIII. METHYLAMINE.

1. Camphoroxalic acid (5 grams = 1 molecule) and methylamine (2.8 grams = 2 molecules) were mixed in alcoholic solution. After evaporation of part of the solvent, colorless needles were deposited; they were purified by recrystallization from alcohol and melted at 172°. With alcoholic ferric chloride no color reaction was produced. Analysis proved the compound to be *methylamine methylcamphoformeneaminecarboxylate*. Analysis:

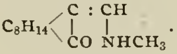
0.2147 gram substance gave 20 cc. N at 14° and 766 mm.

	Calculated for  $C_8H_{14}\langle\begin{matrix}C : CCOONH_3CH_3\\ \vert \quad \vert\\ CO\ NHCH_3\end{matrix}$.	Found.
N	10.51	11.04

2. When treated with sodium hydroxide, the above salt dissolves but, on acidification with dilute hydrochloric acid, decomposes into camphoroxalic acid and methylamine.

3. Upon heating at 175°, methylamine methylcamphoformeneaminecarboxylate gives off methylamine and carbonic anhydride and forms a compound which, when recrystallized from ethyl acetate, melts at 131°. With alcoholic ferric chloride no color reaction is produced. Analysis proved it to be *methylcamphoformeneamine*. Analysis:

0.2131 gram substance gave 13.3 cc. N at 11° and 766 mm.

	Calculated for  $C_8H_{14}\langle\begin{matrix}C : CH\\ \vert \quad \vert\\ CO\ NHCH_3\end{matrix}$.	Found.
N	7.25	7.50

IX. BENZAMIDINE.

Free benzamidine (2.2 grams = 1 molecule) was obtained by dissolving the hydrochloride in absolute alcohol, adding the required amount of potassium hydroxide and filtering off the insoluble potassium chloride. When camphoroxalic acid (5 grams = 1 molecule) is allowed to react with such an alcoholic solution of benzamidine and the solvent is permitted to evaporate spontaneously, a compound is obtained which may be purified by recrystallization from alcohol. It is deposited in colorless prisms; these melt at 184°, evolve a gas, char and decompose. With alcoholic ferric chloride no color reaction is produced and neither acid nor alkali seem to cause any change in the composition of the compound. When heated above its melting-point, it decomposes completely to a carbonaceous mass, from which it is impossible to obtain any definite compound. It did not dissolve in sodium carbonate solution. Analysis proved it to have the empirical formula $C_{19}H_{24}O_4N_2$. Its probable constitution is discussed on p. 231.

0.1539 gram substance gave 0.3723 gram CO_2 and 0.0963 gram H_2O.

0.2147 gram substance gave 15.5 cc. N at 19° and 766 mm.

	Calculated for $C_{19}H_{24}N_2O_4$.	Found.
C	66.27	65.93
H	6.97	7.002
N	8.14	8.30

X. BENZIDINE.

Camphoroxalic acid (5 grams = 1 molecule) and benzidine (4 grams = 1 molecule) were mixed in hot alcoholic solution. When cooled, this deposited a dense mass of greenish-yellow, microscopic needles, which, on account of its very sparing solubility in all the ordinary organic media, was extracted with ether, to remove any camphoroxalic acid and benzidine. The residue, after this treatment, formed a fine powder, which gave no color reaction with alcoholic ferric chloride and was not affected by acids or alkalies. It melts at 190° and, when heated above this temperature, it decomposed to a carbonaceous mass. It is insoluble in sodium carbonate. Analysis proved it to have the empirical formula $C_{24}H_{26}O_3N_2$; its possible constitution is discussed on p. 231.

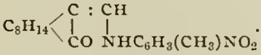
0.1489 gram substance gave 9.4 cc. N at 21° and 775 mm.

	Calculated for $C_{24}H_{26}O_3N_2$.	Found.
N	7.18	7.31

XI. PARANITROORTHOTOLUIDINE.

When camphoroxalic acid (5 grams = 1 molecule) and nitrotoluidine (6.8 grams = 2 molecules) are heated at 150°, under pressure, in alcoholic solution, for 4 hours, a yellow compound is obtained which is purified by recrystallization from alcohol. It is deposited in bright yellow needles, melting at 192°. This compound is unaffected by acids or alkalies, does not dissolve in sodium carbonate and produces no color reaction with ferric chloride, in alcoholic solution. Considerable difficulty was experienced in the combustion of the substance for the determination of nitrogen; even when the heating was done most cautiously, explosions occurred, so that the analytical results were unreliable. These explosions were probably due to the presence of the nitro group in the compound. The difficulty was overcome, in a thoroughly satisfactory manner, by mixing the substance with aluminium powder; under these conditions the nitrogen was evolved during the combustion in a stream which could be easily regulated. Analysis:

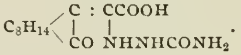
0.2145 gram substance gave 8.8 cc. N at 17° and 765 mm.

	Calculated for  $C_8H_{14}\langle\begin{matrix}C : CH \\ \vert \quad \vert \\ CO \; NHC_6H_3(CH_3)NO_2\end{matrix}$.	Found.
N	4.66	4.79

XII. SEMICARBAZINE.

Semicarbazine hydrochloride (5 grams = 2 molecules) was dissolved in as little cold water as possible and added to an alcoholic solution of potassium acetate (5 grams = 2 molecules); this solution was then mixed with an alcoholic solution of camphoroxalic acid (5 grams = 1 molecule). After evaporation of most of the alcohol on the water-bath the solution was greatly diluted with water; a white, crystalline precipitate was produced which, on purification by recrystallization from alcohol, formed colorless prisms, melting at 200°. When dissolved in boiling glacial acetic acid and precipitated by the addition of alcohol, clusters of colorless, microscopic needles are deposited; these melt at 209°–210° and correspond to the compound described by Bishop Tingle,[1] as one of two substances formed by the action of semicarbazine on potassium camphoroxalate, in alcoholic solution, at 100°, under pressure. The presence of a second compound, stated by him to be deposited from acetone in colorless needles, melting at 218°, was not observed ; it is, apparently, not formed under the conditions employed by us. When the compound melting at 209°–210°, obtained from acetic acid solution, was dissolved in sodium carbonate solution and precipitated by acids it formed a jelly which, after having been dried and recrystallized from acetic acid, had the same melting-point as before, *viz.*, 209°–210°. If the original compound from alcohol, melting at 200°, is recrystallized from acetone, its melting-point remains constant. With alcoholic ferric chloride neither substance produces a color reaction. Both dissolve readily in sodium carbonate and, as has been stated, are precipitated by acids from this solution as colorless jellies. Analysis showed that both compounds have the composition of *semicarbazinecamphoformeneaminecarboxylic acid.*

0.2145 gram substance gave 0.4373 gram CO_2 and 0.1261 gram H_2O.

	Calculated for  $C_8H_{14}\left\langle\begin{array}{l} C : CCOOH \\ \vert \quad\ \vert \\ CO\ NHNHCONH_2 \end{array}\right.$	Found.
C	55.6	55.5
H	6.76	6.57

The possible constitution and relationship of these compounds has been discussed on p. 232.

XII. ORTHOPHENYLENEDIAMINE.

Camphoroxalic acid (5 grams = 1 molecule) and orthophenylenediamine (2.4 grams = 1 molecule) were allowed to react in alcoholic solution. The evaporation of the solvent yielded a deposit of fine yellow needles, which melt at 246°. This substance is identical with the compound obtained by J. Bishop Tingle.[2] The proportional quantities of the reacting materials and the conditions of the experiment were varied, but, in all cases, the same compound was obtained.

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[1] J. Am. Chem. Soc., **23**, 373 (1901).

[2] *Ibid.*, **23**, 375 (1901).

The action of camphoroxalic acid on acetylphenylhydrazine, carbamide, paranitraniline, paramineacetophenone, methylaniline, ethylaniline, benzylaniline, ethylenediamine, benzylphenylhydrazine, quinoline, pyridine, dimethylaniline, orthotoluidine, parabromphenylhydrazine and hydrazine was tried, under conditions similar to those already described for other amines, but in no case could a definite compound be obtained. The reaction-products were usually gummy substances which could not be obtained in a crystalline form. They were heated for some time at 150°–180°, in the hope of forming compounds of the camphoformeneamine type, but from these products also no crystalline derivatives could be isolated by the use of the ordinary organic solvents.

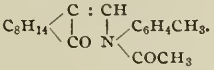
Possibly further investigation of the compounds may result in their purification by distillation, under very low pressures.

ACTION OF ACYLATING AGENTS ON CAMPHOFORMENEAMINE DERIVATIVES.

Paratolylcamphoformeneamine (3 grams = 1 molecule) and acetyl chloride (2.6 grams = 3 molecules) were boiled in solution of anhydrous ether, for about 6 hours; the ether was then evaporated, leaving a compound which crystallized from alcohol in colorless needles, melting at 161°. Analysis showed it to be *acetyl paratolylcamphoformeneamine.*

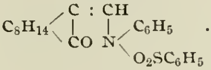
0.1056 gram substance gave 0.2992 gram CO_2 and 0.0705 gram H_2O.

0.5403 gram substance gave 0.0983 gram $Mg_2P_2O_7$ = 0.0747 gram C_2H_3O.

	Calculated for  $C_8H_{14}{<}\begin{matrix}C & : & CH \\ \vert & & \vert \\ CO & & N\end{matrix}{<}\begin{matrix}C_6H_4CH_3. \\ COCH_3\end{matrix}$	Found.
C	77.4	77.26
H	7.74	7.47
CH_3CO	13.78	13.82

Phenylcamphoformeneamine was treated with phenylsulphonic chloride, by the Schotten-Baumann method ; (1 gram = 1 molecule) of phenylcamphoformeneamine was shaken with (1 gram = 7 molecules) of sodium hydroxide, in 10 per cent aqueous solution and (3.5 grams = 5 molecules) of phenylsulphonic chloride, which were added alternately and in small quantities ; a compound is finally obtained which, by crystallization from benzene, is deposited in stout, colorless needles, melting at 133°. Analysis shows it to be *phenylcamphoformeneaminephenylsulphone*.

0.2246 gram substance gave 0.1311 gram $BaSO_4$.

	Calculated for 	Found.
S	8.10	8.07

β-Naphthylcamphoformeneamine (2 grams = 1 molecule) and chloracetyl chloride (2.1 grams = 3 molecules), when boiled for some hours, in anhydrous ether, react to form a bright red substance, which was purified by distillation under diminished pressure. It boiled at 116°, under 45 mm. pressure and condensed to a colorless, crystalline solid, which could be further purified by means of petroleum ether. From this it was deposited in colorless needles, melting at 63°. The compound dissolved in sodium hydrogen carbonate, with evolution of carbonic anhydride and gave no color reaction with ferric chloride. It is very unstable and consequently could not be obtained in a state of purity sufficient to give concordant results on analysis.

The work described in the preceding pages will be continued and extended in various directions. The cost of the greater part of the chemicals which we have used in carrying it out has been defrayed by a grant from the Carnegie Institution ; for this we desire to express our thanks and obligations.

JOHNS HOPKINS UNIVERSITY,
April, 1905.

REVIEWS.

Conversations on Chemistry. First Steps in Chemistry. By W. Ostwald, Professor of Chemistry in the University of Leipzig. Authorized translation by Elizabeth Catherine Ramsay. Part I. General Chemistry. First edition. New York : John Wiley & Sons ; London : Chapman & Hall. 1905. pp. 250. Price, $1.50.

It is difficult to form an opinion of the merits of this book. In some respects it is very good, in others very disappointing. Let us quote at length from the preface :

"By a stroke of good fortune the 'Schule der Chemie' of Stöckhardt, whose memory still lingers among us, was the first text-book of chemistry placed in my hands and it influenced the whole of my subsequent activity in science. Owing to the carefully thought-out directness in presenting the facts to the pupil, the skill in selecting experiments suitable to the physical and mental powers of the beginner, I have never lost touch with experiments, although I have been chiefly occupied with general questions of science. The request of the publishers who used to issue this work that I should write a modern Stöckhardt was both an honor and an opportunity of paying off an old debt of thankfulness."

Ostwald then gives his reasons for thinking that the first lessons in chemistry should be in general chemistry, as underlying inorganic and organic chemistry. He closes the preface by alluding to the dialogue form as seeming "most suitable—while the impression it makes is much more penetrating and lively."

Of the value of Stöckhardt's book the reviewer has no doubt, for a study of it, with laboratory experiments, was of the greatest service to him, as a beginner, in a place where the regular laboratory course was merely analytical. A modern revision of Stöckhardt, appealing, as the original did, to serious students of chemistry, would be a welcome publication.

One may also agree with Ostwald that the first part of such a book should be "general" chemistry.

Ostwald's treatment of the subject—barring the dialogue—is always clear and ingenious and generally shows the master hand. Yet it seems to the reviewer that *the use made in this work* of the dialogue form, renders the book valueless to those who would have profited by Stöckhardt, as it can only appeal to young boys, if indeed it would appeal to them.

Such an opinion of a book by Ostwald requires explanation. Quotations from any page will show that it would not suit a high school boy. Here is a specimen from the chapter on hydrogen :

"Master—You know that iron combines easily with oxygen?

Pupil—Yes, it burns with a lovely rain of sparks.

Master—Now the iron acts on the steam in such a way that it takes the oxygen and combines to form iron oxide; the hydrogen then remains over. Iron oxide is a solid substance even at a red heat and, therefore, remains where the iron was; but hydrogen is a gas and passes further along; it can then be collected over water in the same way as oxygen.

Pupil—That seems very strange to me.

Master—I will give you a simile. Oxygen is a bone which the cat hydrogen had to start with. Then the dog iron comes along and takes the bone from the cat, and the cat hydrogen must run away without the bone."

This is kindergarten talk, but no child and no normal boy under 16 could comprehend the teaching of this book, no matter how colloquial the style.

Here is another specimen, from the same chapter, which illustrates difficulties for reviewer and translator:

"Pupil—You can really blow soap-bubbles with hydrogen?

Master—Yes, and here is a very big one; it separates from the soap-suds and rises like a balloon.

Pupil—Oh, how ripping!"

The difficulty for the reviewer is that we are dealing with the English translation and do not know the Ostwaldian equivalent of "ripping." The difficulty for the translator is that our boys do not speak the same slang as English boys and an American equivalent of this expletive is needed. Perhaps "Say, she's a peach!" would suffice, perhaps not, the problem is difficult. In all seriousness, is it necessary for a master of style, like Ostwald, to do this kind of thing to make a book "penetrating and lively?" E. R.

THE STUDY OF CHEMICAL COMPOSITION. An Account of Its Method and Historical Development, with Illustrative Quotations. By IDA FREUND, Staff Lecturer and Associate of Newnham College, Cambridge. Cambridge Physical Series. Cambridge: University Press. 1904. pp. 650. Price, 18 shillings, net.

The scope of this work may be best shown by giving the headings of the chapters:

Introduction; The Method of the Inductive Sciences. Chapter I., Theories of Combustion. II., Lavoisier and the Law of Conservation of Mass. III., Exact and Approximate Laws. IV., Berthelot and the Law of Mass Action. V., Proust and the Law of Fixed Ratios. VI., Dalton and the Law of Multiple Ratios. VII., Richter and the Law of Equivalent Ratios. VIII., Combining or Equivalent Weights. Symbol Weights. IX., The Ultimate Constitution of Matter. Hypotheses prior to 1800. X., Dalton and the Atomic Hypothesis. XI., Gay-Lussac and the Law of the Combining Volumes of Gases. XII., Avogadro and the Molecular Hypothesis. XIII., Cannizzaro and the Application of Avogadro's Hypothesis to the Determination of Molecular and Atomic Weights. XIV., Petit and Dulong and the Law of Atomic Heat. XV., Mitscherlich and the Connection between Crystalline Form and Chemical Composition. XVI., Mendeléeff and the Periodic Law. XVII., Kekulé and the Law of Valency. XVIII., Berzelius and Isomerism. XIX., The Ultimate Constitution of Matter and the Genesis of the Elements.

The reader is surprised at the omission of the modern theory of solutions, of electrolytic dissociation, of freezing- and boiling-point methods of determining molecular weights and of the phase rule. Indeed, the names of Arrhenius and Willard Gibbs are not in the index. An extract from the preface will explain the author's position :

" * * * I was guided by the following considerations : the kind of historical treatment adhered to throughout the book seemed in this case unsuitable ; space was an object ; and as a matter of fact this subject is adequately dealt with in a number of text-books on physical chemistry, besides which a reprint renders the most important papers accessible."

While the omission is to be regretted in the interest of general readers, it is practically of no importance to the chemists and advanced students to whom this book is addressed. In this country, at least, the student is sure to give as much time to the fascinating study of physical chemistry as is its due and the space available for it in a book of this kind would permit only a brief statement of familiar things.

Miss Freund's method, as may be inferred from the headings, is to give, in each chapter, a detailed account of the work of a pioneer, followed by a careful study of the work of his successors in the particular field to the present time, thus presenting to the reader a charming series of monographs ; yet we find the chapters so connected by cross-references and historical continuity that the book is really "aus einem Guss" and in no sense a series of detached essays. The advantages of this method are obvious. For example, the reader desires to learn about the conservation of mass, he turns to the second chapter and finds the story of Lavoisier's investigations followed by that of Stas and of Morley's work on oxygen and hydrogen, while the next chapter, on "Exact and Approximate Laws," gives a careful study of the results of the work of these three chemists, followed by Lord Rayleigh's work on nitrogen, the researches of Dulong and Arago and of Regnault on the compressibility of air and gases, the relation of the kinetic hypothesis to Boyle's law, Van der Waal's formula and, finally, Landolt's work on the conservation of mass.

In dealing with quantitative researches the author has not "merely stated the final results but has reproduced the values obtained in the actual measurements made, so as to indicate in each case the scope of the work involved and the degree of accuracy obtained."

Furthermore, the author has given "the actual words of those who have announced discoveries, who have described their own experimental investigations, or who have propounded new theoretical views." Thus Chapter IX. consists chiefly of quotations from Aristotle and Lucretius, from Bacon, Descartes, Boyle and Newton. The chapters on Dalton are full of quotations from his letters, his manuscript notes and his "System of Chemical Philosophy."

We have, indeed, a large and increasing number of reprints of important memoirs, but the hard-worked student, with examinations ahead, has little time to read them. If he is wise he will take the time to read and study Miss Freund's book, for nowhere can he find a presentation of the subjects discussed as clear, succinct and scholarly as this and some knowledge of these subjects is imperative.

Reference must be made to the chapter on Mitscherlich and his followers. In this country, the average course of the candidate for the Ph.D. degree, to-day, includes inorganic and organic chemistry, physical chemistry and physics. Few study mineralogy or crystallography. Many students and teachers are ignorant and remain ignorant of the connection between crystalline form and chemical composition. From this chapter of 74 admirably written pages, there is much instruction to be gained.

The last chapter closes with a review of the experimental evidence for the complexity of atoms and the identity of the ultimate constituents, including the work of Ramsey and J. J. Thomson and the work and speculations of Lockyer and Crookes.

Space considerations prevent a more detailed study of this book, but enough has been said to show its importance to all chemists. May it meet the reception it deserves. E. R.

Elektrizität und Materie. Von J. J. Thomson, Mitglied der Royal Society, Professor der Experimental physik an der Universität in Cambridge. Autorisierte Übersetzung von G. Siebert, mit 19 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1904. pp. 100. Price, M. 3.

This is the authorized German translation of the well-known "Yale Lectures" by Prof. Thomson. The subject-matter is the work of this great leader in experimental physics. No one living has thrown as much light on the ultimate nature of matter as J. J. Thomson. We need only recall that, within the last 10 years, our conception of matter has undergone a fundamental change. In his celebrated paper "Die Überwindung des Wissenschaftlichen Materialismus," Ostwald pointed out that *matter is a pure hypothesis*. It was created in the imagination simply as a *carrier of energy*, which is all that we actually know to exist.

Thomson has since shown, by a series of brilliant experiments, that there is no occasion to assume the existence of matter. The *electron*, or unit electrical charge, under the conditions which exist in the atom, has all the properties that we are accustomed to ascribe to matter and there is, therefore, no occasion to assume the existence of what we ordinarily call matter.

These facts are discussed, especially in the fourth and fifth chapters of this book. The sixth and last chapter is devoted to the all-absorbing theme "Radioactivity and Radioactive Substances." These subjects are of as much interest and importance to the physical chemist as to the physicist. Indeed, no man of science, who would keep in touch with the newest and best in physics—the fundamental branch of natural science—can afford to remain unacquainted with this epoch-making work of J. J. Thomson.

The discussion of *valence* is of the greatest importance to the chemist. There is no subject in all chemistry which has been in a more unsatisfactory condition. The vagueness which has characterized the writings on valence for the last 20 years is due to the absence of any definite physical basis upon which to found this whole subject. Thomson points out that all valence is of an electrical nature, in a word, as was developed by the reviewer in his "Physical and Inorganic Chemistry," that the basis of chemical valence is Faraday's Law. With this exact conception as a starting-point, it is safe to predict that we shall hear less in the future of "free bonds" and that some real progress will be made in the consideration of chemical valence.

H. C. J.

ZUR BILDUNG DER OZEANISCHEN SALZABLAGERUNGEN. Von J. H. VAN 'T HOFF. Erstes Heft, mit 34 eingedruckten Abbildungen. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1905. pp. 85. Price, M. 4.

The investigations of van 't Hoff to ascertain the conditions under which the great salt beds of the earth were deposited, are well known. The work has been carried on by van 't Hoff with the co-operation of Meyerhoffer and a number of students and assistants.

The contents of this first *Heft* has to do with crystallization, the effect of time, the effect of temperature, the effect of pressure and applications. This forms a completed chapter, as it were and, therefore, is published in this separate form. When this work, as a whole, is completed it will, undoubtedly, be another monumental contribution to science, to be added to the three which we already owe to van 't Hoff. H. C. J.

JAHRBUCH DER ELEKTROCHEMIE UND ANGEWANDTEN PHYSIKALISCHEN CHEMIE. Berichte über die Fortschritte des Jahres 1903. Herausgegeben von DR. HEINRICH DANNEEL, Privatdocent der physikalischen Chemie und der Elektrochemie der Technischen Hochschule zu Aachen. X Jahrgang. Halle, a. S.: Wilhelm Knapp. 1905. pp. 930. Price, M. 26.

It is only necessary to call attention to the appearance of the tenth annual issue of this valuable "Jahrbuch." This volume gives a complete review of all work that has a bearing on electrochemistry for the year 1903. The book is divided into a scientific and an applied part. The first comprises 529 pages, the latter the remainder of the work.

The reviews are, in general, satisfactorily prepared and the volume, as a whole, is very useful to any one engaged in research in electrochemistry, or who simply desires to follow what is being done by others. H. C. J.

PERCENTAGE TABLES FOR ELEMENTARY ANALYSIS. By LEO F. GUTTMANN, PH.D., A.C.G.I., A.I.C. London: Whittaker & Co.; New York: Macmillan & Co. 1904. Price, $1.00.

This small book of tables is designed to aid one in readily calculating the percentage of carbon and hydrogen in a substance which, upon combustion, yields carbon dioxide and water.

The percentages appear to be worked out with great accuracy as, in several cases, a difference of less than 0.01 and never greater than 0.02 was obtained between the calculated values and those given in these tables.

For any one having a number of combustions to make, the time saved by the use of this book would be a factor well worth taking into account. L. S. TAYLOR.

VOL. XXXIV. OCTOBER, 1905. No. 4.

AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

BROMINE ADDITION COMPOUNDS OF DIMETHYLANILINE.[1]

BY C. LORING JACKSON AND LATHAM CLARKE.

The work described in this paper was begun in January, 1904, and had made much progress before the summer of that year, when we received a paper by K. Fries[2] on the action of bromine on salts of dimethylaniline. At first sight it seemed as if we should be obliged to give up our work to avoid intruding on the field reserved by him, but a more careful comparison of his products with ours showed that they belonged to different series of compounds, for, whereas his substances were perbromides, in which bromine was united to bromine, in ours the bromine was united either to the benzene ring or directly to the nitrogen. We have, therefore, continued our work, but when, in the course of it, we have encountered perbromides, we have dropped the study of them as soon as we had ascertained that they belonged in the field reserved by Dr. Fries.

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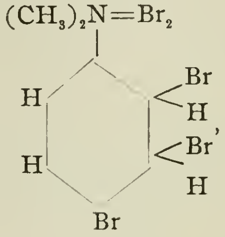
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Latham Clarke.

[2] Ber. d. chem. Ges., **37**, 2338 (1904).

Nomenclature.—Bromine enters into the molecules of the substances described in this paper in four different ways ; it is necessary, therefore, to contrive names to distinguish them, and any such nomenclature must be founded on the usual distinction of brom compounds for those formed by substitution and bromides for those formed by addition. The addition compounds, in which the bromine is attached to the ring, we propose to call benzbromides ; those where it is attached to the nitrogen, amine dibromides (or hydrobromides) ; those where it is attached to bromine, perbromides, as at present. The use of these names is illustrated in that of the following compound,



benzdibromide of dimethylbromphenylamine dibromide—a clumsy name, but one which expresses the constitution as simply as possible.

The perbromides of dimethylaniline, prepared by Fries, are :

$C_6H_4BrN(CH_3)_2HBr_2$,
$C_6H_4BrN(CH_3)_2HBr_3$,
$(C_6H_3Br_2N(CH_3)_2HBr_2)_2Br$,
and $C_6H_3Br_2N(CH_3)_2HBr_3$.

These were prepared by adding bromine to the hydrobromide, or to the free dimethylaniline dissolved in glacial acetic acid. Our compounds were made by adding bromine to dimethylaniline diluted with chloroform ; in this way we obtained the addition of 2, 4 or 6 atoms of bromine and, as there is so little difference in the two methods of preparation, it is necessary first to show that our products belong to a different series from those of Fries.

The structure of our addition compound containing 2 atoms of bromine, which melts at 82°,[1] was determined by the following experiments: By the action of potassic hydrate it is converted into parabromdimethylaniline, melting at 55°, which shows that it is an addition-, not a substitution-product; with ethyl bromide it combines, forming a compound

$$Br_2C_6H_5N(CH_3)_2C_2H_5Br,$$

therefore none of the bromine is attached to the nitrogen atom, but the 2 atoms of bromine must be attached to the benzene ring and the substance is the benzdibromide of dimethylaniline, $Br_2C_6H_5N(CH_3)_2$. This inference is confirmed by the facts, that it dissolves in dilute acids, gives no reaction with potassic iodide and is turned reddish-brown by quinone. We have shown, by experiments soon to be published, that such color reactions with quinone usually indicate a free amine. Further, as parabromdimethylaniline was formed from our dibromide, the 2 atoms of bromine are probably attached to the 3.4 atoms of carbon, although the 1.4 position is not disproved.

Our substance containing 4 atoms of bromine could be made by the action of more bromine on the preceding compound. Under these conditions Fries' perbromide,

$$C_6H_4BrN(CH_3)_2HBr_3,$$

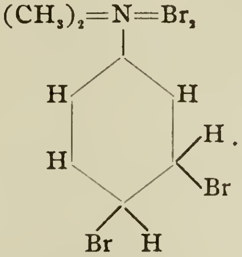
might be formed and our product certainly resembles it in many properties; we will, therefore, first consider whether the two substances are identical. The difference between the melting-points is not great, the perbromide melting at 70°–75°, our compound at 65°–70°; this is not sufficient to establish a difference between unstable bodies like these, which decompose partially during recrystallization and completely on melting. Differences were also observed in color and crystalline form, but they cannot be considered decisive. It is necessary, therefore, to resort to differences in behavior to settle this point and,

[1] The melting-points of all these addition compounds are approximate.

fortunately, the action of our compound with more bromine gives us the desired proof that the two bodies are not the same. Under these conditions it takes up 2 more atoms of bromine, giving a very unstable product with 6 atoms, which loses hydrobromic acid with great ease, dropping to a comparatively stable compound with 5 atoms of bromine. This substance is very close in composition to Fries' perbromide,

$$C_6H_3Br_2N(CH_3)_2HBr_3,$$

but is proved to be different from it by its behavior with sodic acetate in acetic acid, for, whereas the perbromide gives tribrommonomethylaniline, $C_6H_2Br_3NHCH_3$, melting at 37°, hydrobromide, melting at 202°, our substance gives liquid dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2$, hydrobromide, melting at 110°. That they are not identical is also shown by the melting-points, the perbromide melting at 102°, our body at 78°, whereas 5° is the largest inaccuracy in melting-points observed by us as due to the accidental differences in purification or taking of the melting-point frequent with such unstable compounds. As, then, our compound containing 5 atoms of bromine is not identical with that of Fries, our compound with 4 atoms of bromine must also be different from his, since his Br_5 compound is the only one that could be formed from his Br_4 compound. Further, our substance with 4 atoms of bromine cannot be any other perbromide, as it contains only 2 atoms of bromine which act on potassic iodide and the only perbromide of this composition, which could contain that number, is the one described by Fries. The bromine in this compound, then, cannot be attached to bromine, but must be either on the benzene ring or on the nitrogen. Two of the atoms are undoubtedly attached to the benzene ring, as this substance is made from the benzdibromide, which has that structure. The other 2 atoms of bromine cannot be attached to the benzene ring, as they are removed by treatment with potassic iodide (potassic bromide being formed and iodine set free) and bromine on the ring, as in the benzdibromide, does not act on potassic iodide. It follows, therefore, that they must be attached to the nitrogen atom and this conclusion is confirmed by the fact that the compound crystallizes unaltered from ethyl bromide and gives no salt with hydrobromic acid, showing that the nitrogen atom is fully occupied. The substance must be, then, the benz-3,4-dibromide of dimethylphenylamine dibromide,



This constitution is in harmony with the other observed properties of the compound. Quinone gives no color with it. Acetone removes bromine, converting it, apparently, into the benzdibromide of dimethylaniline. Sodic thiosulphate and potassic iodide form parabromdimethylaniline. Sodic hydrate converts it into dibrom dimethylaniline; at first sight the neat formation of a dibrom compound from a substance containing bromine in the side chain might seem strange, but Fries has observed a similar phenomenon with his perbromides, and Chattaway's results[1] would show that all halogen substitutions in the ring of aromatic amines are preceded by substitution in the amino group. Alcohol gives the hydrobromide of dibromdimethylaniline by a similar reaction, followed by addition of hydrobromic acid to the dibromdimethylaniline. When it is allowed to stand in the cold, especially if moistened with chloroform, it is frequently converted, with evolution of hydrobromic acid, into a red substance, which contains 1 atom of bromine capable of replacing iodine in potassic iodide and, from its other properties, is evidently one of Fries' perbromides. Its composition is very near his

$$[C_6H_3Br_2N(CH_3)_2HBr]_2Br,$$

but it is, apparently, a different compound, as it melts at 105° instead of 135°. The way in which such a product could be formed will be considered later. We made no attempt to determine its constitution, as it belongs in the field reserved by Dr. Fries.

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[1] J. Chem. Soc., **15**, 152 (1899).

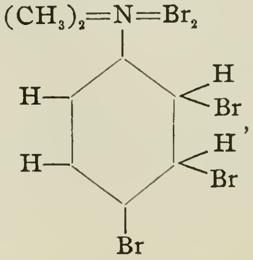
When the body containing 4 atoms of bromine was warmed with chloroform a viscous substance, having nearly the same composition, was produced, which had no action on potassic iodide and was converted, by sodic thiosulphate, into dibromdimethylaniline, it is probably, therefore, the benzdibromide of dimethylbromphenylamine hydrobromide,

$$Br_2C_6H_4BrN(CH_3)_2HBr,$$

and this view is confirmed by the facts that water or sodic hydrate gave with it dibromdimethylaniline, alcohol dibromdimethylaniline hydrobromide. This substance, on standing, acquired the property of acting on potassic iodide, which is caused by its passing into a red compound similar to that described above. We cannot understand, however, how such a body would be formed from $Br_2C_6H_4BrN(CH_3)_2HBr$.

The compound containing 6 atoms of bromine was made by adding bromine to the benz-3,4-dibromide of dimethylphenylamine dibromide. It was so unstable that we could not study it beyond determining its composition, but, from its relation to the other compounds described in this paper, there can be little doubt that it is the benztetrabromide of dimethylphenylamine dibromide, $Br_4C_6H_5N(CH_3)_2Br_2$.

The compound containing 5 atoms of bromine, obtained from the preceding by the removal of 1 molecule of hydrobromic acid, has already been proved to be different from Fries' perbromide, $C_6H_3Br_2N(CH_3)_2HBr_3$, and therefore it cannot be a perbromide at all, because this is the only one of this composition which contains 2 atoms of bromine acting upon potassic iodide. The only possible formula which we can find for it is the following,



so that it is the benzdibromide of dimethylparabromphenylamine dibromide. The para position of the substituted atom of bromine was established by the action of a strong solution of sodic thiosulphate (with potassic iodide), which converted it into parabromdimethylaniline.

The properties of the substance containing 5 atoms of bromine are in harmony with the formula just adopted. Alcohol in quantity or acetone alone (which gave a very violent action) formed the hydrobromide of dibromdimethylaniline, by the conversion of the benzdibromide into a brom compound and hydrobromic acid, which afterwards displaced the 2 atoms of bromine attached to the nitrogen. If the amount of alcohol used was small and the temperature did not rise above 50°, part of this bromine combined with the hydrobromide to give Fries' perbromide,

$$[C_6H_3Br_2N(CH_3)_2HBr]_2Br,$$

the melting-point of which we found at 133°, agreeing, as nearly as could be expected, with 135°, the temperature observed by Fries. The same perbromide seemed to be formed when the substance stood for some time in the air, or when it was treated, under proper conditions, with water, ligroin, or toluene.

Acetone, if diluted with chloroform, removed 2 atoms of bromine from the benzdibromide of dimethylparabromphenylamine dibromide, leaving an oily compound containing 3 atoms of bromine, which did not react with potassic iodide, with potassic hydrate gave dibromdimethylaniline, and with quinone a purplish-black color. These properties indicate that it is a benzdibromide of bromdimethylaniline,

$$Br_2C_6H_4BrN(CH_3)_2.$$

That it is not the hydrobromide of dibromdimethylaniline, which has the same composition, is shown by the reaction with quinone, and its easy solubility in acetone, in which the hydrobromide is nearly insoluble.

Unless there is some flaw in our reasoning, it is established beyond question that two of the substances just described are amine dibromides. So far as we can find they belong to a new class of compounds, none of them being described in the chemical literature unless, indeed, a substance discovered by Raschig[1] should come here. One of the formulas he ascribes to it is $(CH_3)_2NBr_3.2H_2O$, which might be that of an amine dibromide, but, as it not only contains water of crystallization but is made with bromine water, whereas our amine dibromides all are decidedly unstable toward water, we think it probably belongs to a different series. On the other hand, there is no doubt that the compounds $(CH_3)_3NI_2$, discovered by Remsen and Norris,[2] and $(C_3H_7)_3NI_2$, discovered by Norris and Franklin,[3] belong to the same class as our amine dibromides. The compound $(CH_3)_3NICl$, made by Pictet and Krafft[4] may belong here also, although Norris,[5] on repeating their work most carefully, could not obtain this substance, but found that there was formed instead the $(CH_3)_3NI_2$ already mentioned. Dafert's[6] $C_6H_4NON(CH_3)_2I_2$ would be classed with our dibromides, but Bewad's[7] oxide, $(C_2H_5)_3NO$, which at first sight seems remotely related to our substances, can hardly be included with them, as it gives a hydrochloride.

In his work on the amine diiodides Norris used the action of strong sulphuric acid to distinguish between them and the periodides or perbromides which gave an effervescence of the halogen acid, whereas no gas was given off from the diiodides. We confirm this observation in the case of the parabromphenyldimethylamine diiodide, $C_6H_4BrN(CH_3)_2I_2$, melting-point 115°, made by us, but the test was, unfortunately, not applicable to our dibromides, as all of them were also benzdibromides, which give off hydrobromic acid when treated with sulphuric acid.

The two amine dibromides prepared by us show the following characteristic properties: They are reddish-yellow, well-crystallized bodies, from which the 2 atoms of bromine are removed by potassic iodide, potassic hydrate, sodic acetate, sulphurous dioxide, acetone, or aniline, the free amine thus formed being more or less modified by secondary reactions. Alcohol, apparently, acts in the same way, but the amine is converted into the hydrobromide. Many attempts were made to replace the bromine by other radicals, but without success.

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[1] Ber. d. chem. Ges., **18**, 2250 (1885).

[2] THIS JOURNAL, **18**, 90 (1896). The compound $(CH_3)_3NBr_2$, mentioned in this preliminary paper, was proved, on more careful study, to be $(CH_3)_3NHBrBr$. Norris: THIS JOURNAL, **20**, 51 (1898).

[3] THIS JOURNAL, **21**, 499 (1899).

[4] Bull. Soc. Chim., [3], **7**, 74.

[5] THIS JOURNAL, **20**, 51 (1898).

[6] Monats. Chem., **4**, 496.

[7] J. d. Russ. Chem. Ges., **20**, 126. The existence of this substance was confirmed by Lachman, Ber. d. chem. Ges., **32**, 27.

We have also studied the addition of bromine, in chloroform solution, to substituted dimethylanilines. With parabromdimethylaniline we could not obtain a direct addition of 2 atoms of bromine, but this compound, $Br_2C_6H_4BrN(CH_3)_2$, was probably obtained by the action of acetone, diluted with chloroform, on the benzdibromide of dimethylparaphenylamine dibromide, $Br_2C_6H_4BrN(CH_3)_2Br_2$. It was an oil, which, on standing, was gradually converted into the hydrobromide, $C_6H_3Br_2N(CH_3)_2HBr$. The product of the action of bromine on parabromdimethylaniline was the perbromide,

$$C_6H_3Br_2N(CH_3)_2HBr_3,$$

of Fries, not, however, absolutely pure, as it melted at 98° instead of 102°, and gave, with sodic acetate, some dibromdimethylaniline in addition to the normal product, tribrommethylaniline. The formation of this perbromide is to be expected, as probably the benzdibromide of the parabromdimethylaniline would be formed at first and our work indicates that this substance is very unstable, falling easily into dibromdimethylaniline and hydrobromic acid, which would combine to form the hydrobromide and this would then take up the 2 additional atoms of bromine.

The action of bromine on dibromdimethylaniline led only to a substance containing 6 atoms of bromine, compounds with less bromine could not be obtained. This compound gave up 2 atoms of bromine when treated with potassic iodide and sodic thiosulphate, but the organic product was tribrommethylaniline and, as 1 atom of bromine was used in the formation of this substance, it follows that there were really 3 atoms of active bromine. The compound is, therefore, probably the dibromdimethylaniline tetraperbromide, $C_6H_3Br_2N(CH_3)_2HBr_4$, and this view is supported by the facts that it gives hydrobromic acid with sulphuric acid and tribrommethylaniline hydrobromide, $C_6H_2Br_3N(CH_3)H_2Br$, with boiling alcohol or chloroform. As it, therefore, belongs in the field reserved by Dr. Fries we have made no extended study of it.

EXPERIMENTAL.

In order to prepare the addition-compounds described in this paper it was found necessary to purify the materials as follows: The dimethylaniline of the best quality, giving no violet coloration when treated with bleaching-powder, was redistilled, before it was used. The bromine was washed by shaking with water, dried with strong sulphuric acid and redistilled. This purification was necessary in preparing the addition-compounds, but not needed or used in making substitution-products. The chloroform used to dilute the reagents was of an excellent quality. It was dried carefully with calcic chloride and redistilled, after which it was kept in the dark.

Benz-3,4-dibromide of Dimethylaniline, $Br_2C_6H_5N(CH_3)_2$.—A solution of 16.3 grams of bromine, in 50 grams of chloroform, was added, slowly, to 12 grams of dimethylaniline, dissolved in 60 grams of chloroform, the liquid being thoroughly cooled with water during the process. At first the bromine was decolorized almost instantly, but toward the end of the addition the reddish tinge lingered for several minutes. In our first experiments we used more dilute solutions, containing only 10 per cent of the dimethylaniline, but we soon found that as good results could be obtained with 20, or even 30 per cent solutions if sufficient attention was paid to the cooling of the mixture. In any case the success of the operation depended on careful cooling, as, if the temperature was allowed to rise during the reaction, a tarry mass was left on evaporating off the chloroform, from which it was hard to obtain crystals.

After the addition was complete the chloroform was driven off either by distillation *in vacuo* or by passing a stream of dry air through the flask for some hours. The viscid, slightly yellow oil thus obtained usually solidified after standing for a few days, forming long, yellowish plates, which, without further purification, were dried *in vacuo* and analyzed.

0.1559 gram substance gave, by the Carius method, 0.2098 gram AgBr.

	Calculated for $Br_2C_6H_5N(CH_3)_2$.	Found.
Br	56.94	57.24

Properties of Benz-3,4-dibromide of Dimethylaniline.—It usually crystallizes from chloroform in long, slightly yellow plates, but it appears sometimes in long, slender needles, arranged in radiating tufts; sometimes it was impossible to bring the viscous mass to crystallization. A specimen, after being washed with a small amount of chloroform, showed the melting-point 82°. This and the melting-points of similar compounds mentioned in this paper are only approximate numbers, as such unstable substances could not be recrystallized often enough to secure purity and, also, the melting was usually accompanied by decomposition, so that its temperature depended more or less on the conditions of the heating. The dibromide, when exposed to the air, is very slowly converted into parabromdimethylaniline, melting at 55°. It is soluble in ethyl or methyl alcohol, chloroform, or acetone; essentially insoluble in ether, benzene, toluene, ligroin, acetic ester or carbonic tetrachloride. It dissolves in dilute hydrochloric acid, nitric acid, or sulphuric acid, or in strong hydrochloric acid. Strong nitric acid dissolves it easily, but the solution soon turns yellow and then deposits a red oil and a red precipitate, which are soon converted into a yellow oil. Strong sulphuric acid causes an effervescence of hydrobromic acid and the solution soon becomes turbid.

It is decomposed very quickly by water and almost instantly by aqueous or alcoholic potassic hydrate, ammonic hydrate, or aniline, hydrobromic acid being removed with the formation of parabromdimethylaniline, which was purified either by distillation or crystallization from dilute alcohol, when it was identified by its melting-point,[1] 55°, and, for greater certainty, was analyzed:

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[1] Würster and Beran: Ber. d. chem. Ges., **12**, 1820.

0.0420 gram substance gave 0.0398 gram AgBr.

	Calculated for $C_6H_4BrN(CH_3)_2$.	Found.
Br	40.00	40.31

The benz-3,4-dibromide of dimethylaniline adds bromine easily, giving the compounds described later in this paper. With potassic iodide and starch paste it gives no color reaction and with potassic iodide and sodic thiosulphate the product was parabromdimethylaniline. This reaction is mentioned because of its bearing on the results obtained with the substances containing more bromine. With quinone it gives a reddish-brown color.

Benz-3,4-dibromide of Dimethylethylphenylammonic Bromide, $Br_2C_6H_5N(CH_3)_2C_2H_5Br$.—The benzdibromide of dimethylaniline was treated with an excess of ethyl bromide, which at first converted it into an oil that did not mix with the excess of ethyl bromide, but after standing for a few minutes crystals began to appear on the surface of the oil and, after a few hours, it was almost completely converted into white, flat prisms mixed with a small amount of a red substance. These were dried on a porous plate and analyzed without further purification.

0.0663 gram substance gave 0.0955 gram AgBr.

	Calculated for $Br_2C_6H_5N(CH_3)_2C_2H_5Br$.	Found.
Br	61.54	61.27

The crystals are converted at once into a red oil by the addition of water.

The constitution of the benzdibromide of dimethylaniline is established by the experiments just described, as explained in the introduction.

Benz-3,4-dibromide of Dimethylphenylamine Dibromide, $Br_2C_6H_5N(CH_3)_2Br_2$.—To a solution of 12 grams of dimethylaniline, in 120 grams of chloroform, was added, slowly, a solution of 32 grams of bromine, in 100 grams of chloroform. The liquid was exposed to direct sunlight throughout the operation and was cooled with water during the addition of the first half of the bromine, but as soon as the light yellow color of the mixture changed to red the cooling water was removed and the solution allowed to become hot from the heat of the reaction. The addition of the bromine usually took about half an hour and the product was then allowed to stand for an hour longer, after which the solution was evaporated by passing a stream of dry air through it, or better, by distillation *in vacuo*. The thick, red syrup thus obtained solidified, on standing, to a network of reddish needles, which were dried for analysis on a porous plate, in a desiccator, over soft paraffin and sulphuric acid. If the preparation ran properly no hydrobromic acid was given off in the course of it.

I. 0.2569 gram substance gave 0.4423 gram AgBr.
II. 0.1356 gram substance gave 0.2313 gram AgBr.

	Calculated for $Br_2C_6H_5N(CH_3)_2Br_2$.	Found. I.	Found. II.
Br	72.56	73.21	72.61

When this substance was treated with potassic iodide and starch paste, a blue color showed that iodine was set free; accordingly, the amount of bromine which reacted with potassic iodide was determined as follows:[1] A weighed quantity of the substance was treated with 15 cc. of a solution containing 0.5 gram of potassic iodide and 20 cc. of a standard solution of sodic thiosulphate. After the crystals were entirely decomposed, the white, milky liquid was titrated with a standard solution of iodine, to determine how much thiosulphate remained undecomposed. By this method 0.0899 gram substance set free an amount of iodine corresponding to 0.0319 gram Br.

	Calculated for $Br_2C_6H_5N(CH_3)_2Br_2$.	Found.
Active Br_2	36.28	35.48

It follows from this that two of the atoms of bromine react with potassic iodide. If the experiment ran smoothly, the product should be parabromdimethylaniline, formed by the removal of the 2 atoms of active bromine and a molecule of hydrobromic acid ; as a matter of fact, the organic product of a similar experiment, obtained by extraction with ether, consisted principally of parabromdimethylaniline, but also contained a very small amount of dibromdimethylaniline.

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[1] This method is founded on one in Sutton's "Volumetric Analysis," 7th Edition, p. 129.

Ethyl bromide dissolved the substance, but it crystallized out unchanged from this solution. The observations just described prove that the substance is the benz-3,4-dibromide of dimethylphenylamine dibromide, $Br_2C_6H_5N(CH_3)_2Br_2$, as explained in the introduction. This compound was also prepared by the action of more bromine on the benzdibromide of dimethylaniline, dissolved in chloroform.

Properties of the Benz-3,4-dibromide of Dimethylphenylamine Dibromide.—It forms long, yellowish-red needles, which appear red if seen in large masses. The melting-point was not sharp, as the melting usually took place at 65°–70°, but occasionally a specimen was obtained which melted at 68°. It is soluble in ethyl or methyl alcohol, chloroform, acetone, or ethyl acetate ; somewhat soluble in tetrachloride of carbon ; essentially insoluble in benzene, toluene, or ligroin. All of these solvents, except chloroform and tetrachloride of carbon, react with the substance in the cold. It can be recrystallized from chloroform at ordinary temperatures, but if heated with it a reaction sets in. The various actions of these solvents are described later in the paper. Strong nitric acid dissolves it only partially and the mixture turns brown and turbid after a few minutes ; strong sulphuric acid dissolves it with evolution of hydrobromic acid. It is insoluble in dilute acids, whereas the benzdibromide of dimethylaniline dissolves in them. Aqueous or alcoholic potassic hydrate converts it into dibromdimethylaniline.

Action of Acetone on Benz-3,4-dibromide of Dimethylphenylamine Dibromide.—A strong solution of 1 gram of the substance, in chloroform, was treated, slowly, with acetone until it was decolorized. The solution was then warmed on the water-bath and the solvents removed by means of a current of dry air, after which the oily residue, that smelt distinctly of bromacetone, was allowed to stand *in vacuo* until this odor had disappeared. Although it did not solidify so that the melting-point could be determined, we are of the opinion that it was the benz-3,4-dibromide of dimethylaniline, on account of the following reactions: Quinone gave the characteristic color and alkalies, or even water removed hydrobromic acid from it (detected by argentic nitrate) and formed parabromdimethylaniline, recognized by its odor, color reaction with quinone and melting-point, 55°.

Action of Ethyl Alcohol on Benz-3,4-dibromide of Dimethylphenylamine Dibromide.—When the substance was boiled with alcohol the solution was decolorized in a few minutes and the colorless liquid deposited, on evaporation, the hydrobromide of dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2HBr$, recognized by its melting-point, 110° (see later). Cold alcohol produced the same effect in 2–3 weeks; in this case the hydrobromide is deposited in beautiful, large, square plates.

Action of Benz-3,4-dibromide of Dimethylphenylamine Dibromide with Hot Chloroform.—One gram of the substance was boiled with 10 cc. of chloroform, on the water-bath, in a flask with a return-condenser, for 2 hours, at the end of which time the color of the solution had changed from red to yellow. A small amount of hydrobromic acid was given off, due probably to a secondary reaction; if the boiling was continued still longer, more hydrobromic acid was evolved and a red body, containing less bromine than the original substance, was formed; it, therefore, should not be continued beyond 2 hours. The yellow solution obtained in this time was freed from chloroform by warming it on the water-bath, in a current of dry air, when a yellowish oil was left, which we could not bring to solidification; it was, accordingly, dried *in vacuo* and analyzed. The two specimens analyzed proceeded from different preparations:

I. 0.1091 gram substance gave 0.1850 gram AgBr.
II. 0.1029 gram substance gave 0.1749 gram AgBr.

	Calculated for $C_8H_{11}NBr_4$.	Found. I.	Found. II.
Br	72.56	72.18	72.35

The constancy in composition shown by these analyses indicates that the substance is a definite compound, in spite of its unsatisfactory physical properties, and also that it is isomeric, or nearly so, with the substance from which it was formed. It sets free no iodine from potassic iodide, but after standing for a few days it gains the power of doing this. Longer standing converts it into a red body, probably identical with that described in the next section. With alcohol, acetone, or acetic ester it yielded dibromdimethylaniline hydrobromide, melting-point 110°, while aqueous potassic hydrate gave dibromdimethylaniline. It is soluble in chloroform, but essentially insoluble in ether, toluene, or tetrachloride of carbon. Its most probable constitution is discussed in the introduction.

Decomposition of Benz-3,4-dibromide of Dimethylphenylamine Dibromide when Moistened with Chloroform.—When the substance, moistened with chloroform, was allowed to stand in a corked flask it slowly changed to a mass of brown-black plates. The formation of this dark substance was promoted by rubbing with a glass rod, or better still, by inoculation with some of the plates from a previous preparation. The dry dibromide also, sometimes, was converted spontaneously into this product, which then appeared as a reddish-black powder, but this action took place much more slowly than when the compound was moistened with chloroform. The substance was hard to obtain, as the change did not take place invariably and we have not succeeded in finding the conditions necessary to make certain of its preparation. It was dried in a desiccator, over soft paraffin and sulphuric acid :

0.1823 gram substance gave 0.3000 gram AgBr.

	Calculated for $C_{16}H_{24}N_2Br_7$.	Found.
Br	69.56	70.02

The substance sets free iodine from iodide of potassium, the amount of which was determined as follows :

0.1695 gram substance set free 0.0249 gram I.

	Calculated for $C_{16}H_{24}N_2Br_7$.	Found,
Br	9.96	9.19

That is, only one of the atoms of bromine can replace iodine in potassic iodide. These results and the brownish-black color, show that the body is a perbromide similar to those discovered by Fries,[1] and we therefore did not pursue the study of it. The sample analyzed melted at 105°.

Dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2$.—This substance was frequently obtained in the course of our work on the benz-3,4-dibromide of dimethylphenylamine dibromide. It was most conveniently made from the oil left after evaporating off the chloroform in the preparation of this body. This oil was treated with an aqueous solution of potassic hydrate, the product extracted with ether and, after distilling off the ether, the residue was dried and distilled under ordinary pressure. Care should be taken that a sufficient amount of potassic hydrate was used, as the presence of dibromdimethylaniline hydrobromide produced explosions during the distillation. Parabromdimethylaniline boils at about the same temperature (264°) as the dibrom compound; it is wise, therefore, to use enough bromine in the preparation of the original oil to make certain that all the benzdibromide of dimethylaniline should take up at least two more atoms of bromine. If parabromdimethylaniline was found to be present in the product, it could be removed, in great measure, by allowing the mixture to stand for 2 or 3 weeks, when most of the monobrom compound crystallized out. The yield of dibromdimethylaniline was very good, averaging 85–95 per cent of the theory.

0.3532 gram substance gave 0.4777 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2$.	Found.
Br	57.34	57.55

Properties of Dibromdimethylaniline.—We found the boiling-point of this liquid 264°, at 760 mm. This is somewhat lower than the boiling-point 275°, at 746 mm., found by Fries[1] for his *o,p*-dibromdimethylaniline, but we feel no doubt in regard to the identity of the two compounds, as Fries purified his product by conversion into the tin salt, whereas ours was only submitted to distillation and, therefore, the lower boiling-point found by us is undoubtedly due to a quantity of impurity too small to be shown by our analysis. His boiling-point should be adopted as the correct one. It is a colorless, oily liquid, which mixes with ethyl or methyl alcohol, ether, benzene, toluene, chloroform, acetone, or ethyl acetate, but not with water. It is soluble in moderately strong acids, takes up bromine to form a compound described later, combines with methyl iodide or ethyl bromide to form ammonium compounds, and gives a violet color with quinone.

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[1] Ber. d. chem. Ges., 37, 2338 (1904).

Hydrobromide of Dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2HBr$.—This substance appeared frequently as a decomposition-product of the addition-compounds described in this paper. It can be made easily as follows: The benz-3,4-dibromide of dimethylphenylamine dibromide, which can be used in the viscous state, as first obtained, was treated with dilute alcoholic potassic hydrate, in small portions at a time, until the color was just discharged; the potassic bromide was then filtered out and the alcoholic filtrate evaporated on the water-bath until the product began to crystallize. It was also made by passing dry hydrobromic acid into a solution of dibromdimethylaniline, when it appeared as a white precipitate. It was purified by recrystallization once from alcohol and several times from acetone, until it showed the constant melting-point 110°, when it was dried *in vacuo* and analyzed:

I. 0.1011 gram substance gave 0.1594 gram AgBr.
II. 0.2137 gram substance gave 0.3355 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBr$.	Found. I.	Found. II.
Br	66.66	67.07	66.80

Properties of Dibromdimethylaniline Hydrobromide.—It crystallizes from alcohol in colorless, square plates; from chloroform in cubes modified by many other planes; from acetone in cubical forms, often with hollows in the sides, as in some crystals of salt. It melts at 110° to a clear, colorless liquid and, if heated to 140°, is suddenly converted into a blue coloring-matter. It is soluble in alcohol or chloroform; fairly soluble in warm ether, nearly insoluble in cold; very slightly soluble in acetone ; essentially insoluble in benzene, toluene, acetic ester, or carbonic tetrachloride. The strong mineral acids dissolve it easily. An alkali or even water decomposes it at once, dibromdimethylaniline being formed, but it can be boiled with alcohol for several hours without decomposition.

Benztetrabromide of Dimethylphenylamine Dibromide, $Br_4C_6H_5N(CH_3)_2Br_2$.—This substance, which contained more bromine than any other prepared by us, was obtained with difficulty because of its strong tendency to lose hydrobromic acid and form the benzdibromide of dimethylbromphenylamine dibromide, which is described later. The body containing 6 atoms of bromine was prepared as follows : A solution of 4.8 grams of bromine, in 24 grams of chloroform, was added, slowly, to a solution of 1.2 grams of dimethylaniline in 6 grams of chloroform, the mixture was cooled from the first with ice-water and exposed to direct sunlight. The red solution thus obtained was allowed to stand for more than 2 days, at ordinary temperatures, after which the chloroform was distilled off *in vacuo* and the thick, red liquid thus obtained deposited small, reddish crystals of the substance, after standing a few minutes.

0.1286 gram substance gave 0.2386 gram AgBr.

	Calculated for $Br_4C_6H_5N(CH_3)_2Br_2$.	Found.
Br	79.86	78.96

The compound appears in small, reddish needles and is very unstable, splitting off hydrobromic acid to form the body with 5 atoms of bromine (described next) so that the hexabrom compound usually was not the product of the preparation described above, but was obtained only when the utmost care was exercised to exclude every trace of moisture. It also gives off 1 molecule of hydrobromic acid when heated, so no attempt was made to determine its melting-point.

Benzdibromide of Dimethylbromphenylamine Dibromide, $Br_2C_6H_4BrN(CH_3)_2Br_2$.—The method for preparing this substance was essentially the same as that given for the preceding compound, except that no extraordinary precautions were taken. We used 12 grams of dimethylaniline, dissolved in 120 grams of chloroform, and 48 grams of bromine, dissolved in 120 grams of chloroform. The solution of bromine was added slowly to that of the dimethylaniline, the mixture being cooled with ice-water during the addition of the first third of the bromine, as otherwise the reaction became too violent. After that the remainder of the bromine was added without cooling and the mixture finally warmed on the water-bath, for 2 hours. We carried on our earlier preparations in sunlight, but later experiments showed that this was unnecessary. The reddish liquid thus obtained was freed from chloroform by distillation, at first at ordinary pressure, finally *in vacuo*, and the thick, oily residue allowed to stand, at ordinary temperatures, for 2–3 days, when it solidified to a mass of large crystals. These were dried for analysis, first on a porous plate, later in a desiccator over soft paraffin :

I. 0.3674 gram substance gave 0.6636 gram AgBr.
II. 0.1861 gram substance gave 0.3345 gram AgBr.

	Calculated for $C_6H_4Br_3N(CH_3)_2Br_2$.	Found.	
		I.	II.
Br	76.92	76.85	76.52

0.6675 gram substance gave with KI and $Na_2S_2O_3$ 0.1960 gram active Br.

	Calculated for $C_6H_4Br_3N(CH_3)_2Br_2$.	Found.
2Br	30.77	29.33

Properties of the Benzdibromide of Dimethylbromphenylamine Dibromide.—It forms large, well-formed, long, reddish prisms, terminated by a single plane at an oblique angle. Smaller crystals are yellow. On standing in the air it slowly turns to a reddish-black powder. It melts at 78°, but when the melted substance is heated to a higher temperature it begins to decompose, giving off white fumes which condense on the upper part of the tube to a colorless liquid, soon crystallizing in needles. The residue left in the bottom of the tube has a violet color. Neither of these substances was studied further. It seems not to be decomposed by chloroform, in which it is soluble, or tetrachloride of carbon, in which it is very slightly soluble, but all other solvents tried decomposed it in the ways described later in this paper. When heated with water, it turns black, forming, probably, the same product as with air. Strong hydrochloric acid dissolves it, apparently unchanged; strong nitric acid dissolves it, forming a yellow solution which soon grows brown and turbid; strong sulphuric acid partially dissolves it with an effervescence of hydrobromic acid. Aqueous or alcoholic potassic hydrate converts it into dibromdimethylaniline. When the substance is fused for several minutes with symmetrical tribromaniline a red body is formed; fusion with quinone gives a red, with pyrocatechin a brown and with tetrabrompyrocatechin a red product; none of these reagents act on it in solution and as these products seemed to be due to a decomposition of the substance we did not pursue this part of the research further.

Action of Acetone on the Benzdibromide of Dimethylbromphenylamine Dibromide.—Acetone acted so violently on this substance that the product was a black, tarry mass, the formation of which was accompanied by that of bromacetone, to judge from the effect on the eyes. The tar, after standing 2–3 weeks, deposited well-formed, square crystals of dibromdimethylaniline hydrobromide, recognized by its melting-point, 110°, and some dibromdimethylaniline was detected in the pasty mass in which the crystals were embedded.

If, instead of using pure acetone, it was used diluted with chloroform, a different result was obtained. One gram of benzdibromide of dimethylbromphenylamine dibromide was dissolved in 10 cc. of chloroform and acetone added in small portions at a time, with vigorous shaking between each addition, until the solution was decolorized. The liquid was then concentrated on the water-bath to a volume of about 3 cc. and the drying was finished *in vacuo* over glycerol, which, in 1 night, removed the odor of the bromacetone. As the residue refused to solidify, it was analyzed as it stood. The two analyses were made with different preparations:

I. 0.0912 gram substance gave 0.1396 gram AgBr.
II. 0.1435 gram substance gave 0.2195 gram AgBr.

	Calculated for $Br_2C_6H_4BrN(CH_3)_2$.	Found. I.	II.
Br	66.66	65.12	65.06

These results are as near as could be expected from such a body. It is an oil, which had a dark color, as obtained by us, but is probably colorless when pure. It mixes freely with acetone, gives no reaction with potassic iodide and starch, but a purplish-black color with quinone. Aqueous potassic hydrate converts it into dibromdimethylaniline, with loss of hydrobromic acid. These properties show that it is probably the benzdibromide of bromdimethylaniline, $Br_2C_6H_4BrN(CH_3)_2$, as explained in the introduction. It is isomeric with the dibromdimethylaniline hydrobromide, $C_6H_3Br_2N(CH_3)_2HBr$, into which it is converted after standing for several days.

Action of Alcohol on the Benzdibromide of Dimethylbromphenylamine Dibromide.—If the substance was boiled with alcohol for some minutes the red color was discharged and dibromdimethylaniline hydrobromide was formed; the same reaction took place when it was allowed to stand several weeks, with an excess of alcohol, at ordinary temperatures, but a different result was obtained when it was heated to 50° with just enough alcohol to dissolve it, then, on cooling, a voluminous precipitate of glistening black plates was deposited. The same substance appeared in the form of large, black prisms, when a cold, concentrated alcoholic solution was allowed to evaporate spontaneously; the prisms began to form in 2–5 hours, were at their best in 12–20 hours, and began to decompose after 24 hours. It was dried, for analysis, on a porous plate in a desiccator:

I. 0.0744 gram substance gave 0.1235 gram AgBr.
II. 0.2112 gram substance gave 0.3495 gram AgBr.

	Calculated for $C_{16}H_{20}N_2Br_7$.	Found. I.	II.
Br	70.00	70.61	70.42

The amount of bromine which can set free iodine from potassic iodide was determined:

0.3492 gram substance gave 0.0374 gram Br.

	Calculated for $C_{16}H_{20}N_2Br_7$.	Found.
Br_1	11.43	10.70

The amount of hydrobromic acid was also determined which was removed from the body by the action of water, the secondary product being dibromdimethylaniline :

0.1207 gram substance gave 0.0851 gram AgBr.

	Calculated for $C_{16}H_{20}N_2Br_7$.	Found.
Br_3	30.00	30.00

These data show that the substance is a perbromide and, as it melted at 133°, it is probably identical with Fries'

$$[C_6H_3Br_2N(CH_3)_2HBr]_2Br,$$

which melts at 135°.

Toluene, when shaken for 40 hours with the benzdibromide of dimethylbromphenylamine dibromide, converts it into the perbromide melting at 133°, described above, and ligroin has the same effect when allowed to stand with it. In each case the liquid takes up bromine.

Action of Aniline on Benzdibromide of Dimethylbromphenylamine Dibromide.—The principal products of this reaction were aniline hydrobromide and dibromdimethylaniline, whether the reagents were dissolved in chloroform or mixed undiluted. In the latter case, in 3 experiments out of 10 or more tried by us, we obtained small quantities of red crystals, amounting to not more than 1 per cent of the dibromide used. As we could not find the conditions under which these crystals were formed, this part of the work was abandoned. They may be analogous to the benzidine compound observed by Fries.

Action of Potassic Iodide on Benzdibromide of Dimethylparabromphenylamine Dibromide.—This reaction was of importance, as on it was founded one of our methods of analysis. A dilute solution of potassic iodide, when mixed with our compound, at once developed a reddish color from the iodine set free, as was proved by the reaction with starch paste. If the amount of free iodine was determined at once, with sodic thiosulphate, constant results were obtained, but if the mixture containing the free iodine was allowed to stand, it was found that it gradually went into combination again, so, to get good results from this analytical process, the potassic iodide should be added mixed with a known excess of thiosulphate, and the amount of thiosulphate, remaining after the action, determined.

The organic product of the action of potassic iodide and sodic thiosulphate was determined by the following experiment: Three grams of benzdibromide of dimethylbromphenylamine dibromide were added to a solution of 10 grams of potassic iodide and 10 grams of sodic thiosulphate, in 200 cc. of water. The mixture was shaken thoroughly and allowed to stand for 2 hours, after which it was extracted with ether. The extract distilled over at 264° and had the odor of dibromdimethylaniline; it also gave the characteristic color with quinone. For greater certainty it was analyzed:

0.2941 gram substance gave 0.3919 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2$.	Found.
Br	57.34	56.72

The aqueous solution, left after the extraction with ether, contained no sulphur and did not smell of sulphurous dioxide.

When a much stronger solution of the iodide and thiosulphate was used, a precipitate of sulphur was formed soon after the materials were mixed and there was a strong odor of sulphurous dioxide. The ether extract, in this case, consisted of much parabromdimethylaniline mixed with less dibromdimethylaniline. The parabrom compound was evidently formed by the direct removal of all the added bromine by the reducing agent. The bearing of this experiment on the constitution of the substance is discussed in the introduction.

If a solution of benzdibromide of dimethylparabromphenylamine dibromide, in chloroform, was treated with solid potassic iodide, a new substance was formed crystallizing in reddish-yellow, flat prisms, with square ends and melting at 137°. This compound was prepared as follows: The concentrated chloroform solution of the dibromide, obtained in its preparation by evaporating off the excess of chloroform, was used. To this was added one-fourth of its weight of pulverized potassic iodide and, after a few minutes, twice its volume of alcohol. After standing for 10 minutes the mixture was treated with distilled water, which was added, drop by drop, on the edge of the beaker, until the dirty brown precipitate formed at first just dissolved on shaking. The liquid was then decanted as quickly as possible from the solid potassic iodide and in 1–2 minutes it became nearly solid, from the deposition of a network of beautiful, reddish-yellow needles. The beaker was allowed to stand several minutes, to secure complete precipitation, and then the solid was filtered out and recrystallized from alcohol until it showed the constant melting-point 137°.

0.1724 gram substance gave, on combustion, 0.1251 gram CO_2 and 0.0425 gram H_2O.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBrI$.	Found.
C	19.72	19.79
H	2.05	2.74

0.1615 gram substance, treated with sodic thiosulphate and potassic iodide, showed 0.0374 gram active I.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBrI$.	Found.
I	26.33	23.16

This result, although not very exact, shows that the atom of iodine was loosely attached. Quinone or ethyl bromide had no effect on it; aqueous potassic hydrate gave dibromdimethylaniline. From these observations it can be inferred that the iodine is attached to the bromine of a hydrobromide; the substance, therefore, belongs to the same class as the perbromides and falls outside of the field of our research. It seems evident that the loss of free iodine observed in our analytical work on amine dibromides, when the iodine was allowed to stand with the amine, was due to the formation of a compound similar to this.

Action of Sodic Acetate on Benzdibromide of Dimethylparabromphenylamine Dibromide.—Pulverized, anhydrous sodic acetate was added to a solution of 1 gram of the dibromide, in 10 cc. of glacial acetic acid, until the color was completely discharged. The solution was then neutralized with dilute sodic hydrate and extracted with ether. The extract was an oil, which had the odor of dibromdimethylaniline and gave, with quinone, the proper color reaction. Its identity was established by treating it with gaseous hydrobromic acid, which converted it into the hydrobromide, $C_6H_3Br_2N(CH_3)_2HBr$, melting at 110°.

The Addition of Bromine to Parabromdimethylaniline. — A number of attempts to obtain a product formed by the addition of 2 atoms of bromine to parabromdimethylaniline led to no favorable result. Usually a red substance was formed, probably Fries' $[C_6H_3Br_2N(CH_3)_2HBr]_2Br$, or else the following compound, containing 5 atoms of bromine, was formed, and part of the parabromdimethylaniline remained unaltered. On one occasion we thought we obtained the desired substance, but the amount was too small to identify it with certainty. Although this substance could not be made directly from parabromdimethylaniline, we probably obtained it, as already stated, by the action of acetone, diluted with chloroform, on the benzdibromide of dimethylparabromphenylamine dibromide.

A substance containing 5 atoms of bromine was obtained, without difficulty, by adding 16 grams of bromine, dissolved in 100 grams of chloroform, to 10 grams of parabromdimethylaniline, dissolved in 100 grams of chloroform; on evaporation *in vacuo* the substance was obtained in slender, reddish-brown prisms, which melted at 98°.

0.1643 gram substance gave 0.2989 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBr_3$.	Found.
Br	76.92	77.43

This substance is, without doubt, principally Fries' dibromdimethylaniline perbromide, which melts at 102° and corresponds to it in its other properties. The somewhat lower melting-point of our preparation indicates, however, that it was not perfectly pure and this is confirmed by the fact that sodic acetate gave some dibromdimethylaniline with our specimen, in addition to the tribrommethylaniline which is the normal product with Fries' compound. That his substance would be the most probable product in this case is explained in the introduction.

The Addition of Bromine to Dibromdimethylaniline.—All our attempts to prepare a compound containing 4 atoms of bromine in this case led to no result, but one containing 6 atoms of bromine was prepared as follows: Six and four-tenths grams of bromine, dissolved in 30 grams of chloroform, were added, slowly, to 5.6 grams of dibromdimethylaniline, dissolved in 50 grams of chloroform. The bromine was decolorized almost as fast as it was added and little heat was evolved. On standing over night the new compound crystallized out in reddish prisms, which were dried *in vacuo* for analysis:

0.3050 gram substance gave 0.5695 gram AgBr.

	Calculated for $C_6H_3Br_2N(CH_3)_2HBr_4$.	Found.
Br	80.00	79.45

0.5551 gram substance contained 0.1589 gram active Br.

	Calculated for $C_6H_5Br_2N(CH_3)_2HBr_4$.	Found.
2Br	26.67	28.64

This result seems, at first sight, to indicate that the substance contains 2 atoms of active bromine, but, as the organic product is tribrommethylaniline, 1 atom of bromine has been used up in making this substance and, in fact, there are 3 atoms of active bromine. The substance, therefore, is probably a perbromide, $C_6H_3Br_2N(CH_3)_2HBr_4$, of a different class from any of those obtained by Fries from dimethylaniline. This inference is supported by its properties. It crystallizes in yellowish-red, flat prisms, so small that they look like needles, melting at 98°. Strong sulphuric acid causes an effervescence, which consists, in part, of hydrobromic acid. Boiling alcohol or chloroform converted it into tribrommethylaniline hydrobromide, $C_6H_2Br_3NHCH_3HBr$, which is described below. Acetone gave the hydrobromide of dibromdimethylaniline, recognized by its melting-point, 110°. Potassic hydrate gave dibromdimethylaniline. With cold alcohol it formed Fries' perbromide, $[C_6H_3Br_2N(CH_3)_2HBr]_2Br$, melting at 135°.

Hydrobromide of Tribrommethylaniline, $C_6H_2Br_3NHCH_3HBr$.—Three grams of the dibromdimethylaniline tetraperbromide, mentioned above, were boiled, on the water-bath, with 30 cc. of alcohol, until the red color had disappeared. The colorless solution, on cooling, deposited a white crystalline precipitate, which, after washing with a little chloroform and 2 or 3 recrystallizations from that solvent, appeared in cubes or closely related forms. It turned brown at about 200° and melted at 202° to a black liquid.

I. 0.2133 gram substance gave 0.3744 gram AgBr.
II. 0.1253 gram substance gave 0.2244 gram AgBr.

	Calculated for $C_6H_2Br_3NHCH_3HBr$.	Found. I.	II.
Br	75.46	74.71	76.21

That it is the hydrobromide of tribrommethylaniline was proved by treating it with water, which decomposed it into hydrobromic acid and tribrommethylaniline, $C_6H_2Br_3NHCH_3$, recognized by its melting-point,[1] 37°. With the hydrobromide of tribrommethylaniline some dibromdimethylaniline was also formed, which was removed by the crystallization from chloroform. Boiling chloroform also gave the hydrobromide.

Properties of the Hydrobromide of Tribrommethylaniline, $C_6H_2Br_3NHCH_3HBr$.—It crystallizes in white cubes or in similar forms, modified by many planes. It turns brown at 200° and melts, to a black liquid, at 202°. It is somewhat soluble in acetone or hot chloroform; nearly insoluble in benzene, toluene, ethyl acetate, or carbonic tetrachloride. Its behavior with water has been mentioned already.

Parabromphenyldimethylamine Diiodide, $C_6H_4BrN(CH_3)_2I_2$.—This compound was made by adding a hot solution of 2.6 grams of iodine, in 25 grams of chloroform, to 2 grams of parabromdimethylaniline, dissolved in 10 grams of chloroform. The almost black mixture deposited crystals of the new compound as it cooled. These were dried on a tile, in a desiccator, for analysis:

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[1] Fries: Ber. d. chem. Ges., **37**, 2338 (1904).

0.2521 gram substance gave 0.3736 gram AgBr + AgI.

	Calculated for $C_6H_4BrN(CH_3)_2I_2$.	Found.
Br + I	73.55	75.21

This result, bad as it is, shows the substance can have no other formula.

0.2102 gram substance lost 0.1154 gram I when treated with $Na_2S_2O_3$ and KI.

	Calculated for $C_6H_4BrN(CH_3)_2I_2$.	Found.
I_2	55.94	54.91

Properties of the Parabromphenyldimethylamine Diiodide.—It forms black, flat prisms, melting at 115°. It is slightly soluble in alcohol, acetone, or acetic ester, giving green solutions; benzene, toluene, ligroin, or carbonic tetrachloride does not dissolve it, but the solvent slowly takes on a reddish color from the removal of a part of the iodine from the compound. An aqueous solution of potassic iodide removes a considerable amount of iodine, as was shown by the starch paste test. Ethyl bromide has no action upon the compound. Strong sulphuric acid gives no effervescence with it. A number of attempts to replace the iodine with other radicals led to no successful result.

CAMBRIDGE, MASS.,
May 4, 1904.

POSTSCRIPT.—Two months after the manuscript of the foregoing paper had been sent to the editor of this JOURNAL, that is on July 3rd, we received a paper by A. Hantzsch and W. Graf[1] on the same subject, in which they describe the dimethylparabromphenylamine dibromide, $C_6H_4BrN(CH_3)_2Br_2$, prepared by them, without difficulty, from parabromdimethylaniline, whereas, of the many experiments of this sort tried by us only one gave this product, and that not in quantity sufficient for identification. On the other hand, they were unable to obtain stable addition-compounds of unsubstituted dimethylaniline under any conditions, whereas we had no trouble in preparing the di-, tetra- and hexabromide described above. Oddly enough, therefore, the two papers supplement each other, and together give a nearly complete account of these compounds. The nature of the slight differences in procedure which led to these different results can be only a matter of conjecture at present.

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[1] Ber. d. chem. Ges., **38**, 2154 (1905).

The sketch of the history of the subject given in our paper should be modified according to the newer work in the paper of Hantzsch and Graf.

August 18, 1905.

THE APPROXIMATE COMPOSITION OF THE HYDRATES FORMED BY A NUMBER OF ELECTROLYTES IN AQUEOUS SOLUTIONS; TOGETHER WITH A BRIEF GENERAL DISCUSSION OF THE RESULTS THUS FAR OBTAINED.

[THIRTEENTH PAPER.]

This investigation, like the preceding eight in this field, was carried out under a grant from the Carnegie Institution.

By Harry C. Jones and H. P. Bassett.

A number of lines of evidence bearing upon the question of dissolved substances combining with the solvent, have been considered in preceding papers. Certain comparatively new lines will be taken up in this one. Dr. G. N. Lewis, of Harvard, called my attention to various color changes that seem to have a direct bearing upon the problem in question. He has informed me, by private letter from the Government Laboratories in the Philippines, where he is now stationed, that his own observations will soon be published in the *Zeitschrift für physikalische Chemie*, and has kindly permitted me to refer to them in advance. The experiments described below consist of modifications of the reactions pointed out by Dr. Lewis, together with a number of additional color changes.

When cobalt chloride, with its 6 molecules of water of crystallization, is dehydrated, either wholly or in part, there is, as is well known, a marked color change from the typical reddish color of the solution to a beautiful blue. This change in color can be readily effected, in solution, by a number of substances. The fact has long been known, but its bearing on the theory of hydrates in solution, as advocated by Jones, has been pointed out only once, and that in a recent[1] paper by this author.

If, to a fairly concentrated solution of cobalt chloride, a comparatively small amount of fused calcium chloride is added, the blue color quickly makes its appearance. Since the earlier investigations of Jones and Getman[2] have shown that aluminium chloride has even greater hydrating power than calcium chloride, we should expect a smaller quantity of aluminium chloride to effect the same color change. Such is the fact.

If crystallized calcium chloride is added to a fairly concentrated solution of cobalt chloride, the blue color does not appear at first, but after adding a large amount of the crystallized salt and vigorously shaking, the blue color gradually appears and finally becomes quite intense. This shows beyond question, to our minds, that calcium chloride, with 6 molecules of water of crystallization, can, in solution, combine with a still larger quantity of water, as is demonstrated by a partial dehydration of the cobalt chloride and the consequent blue color.

About the only reasonable objection that could be offered to our conclusion from this experiment is that, in the above cases, there is a double chloride formed which has a blue color. The number of lines of evidence against this conclusion is so large as to render it entirely untenable. In the first place, it was shown some years ago by Jones and Ota[3] and by Jones and Knight[4] that double chlorides, even in concentrated solutions, could not exist, to any great extent, as such, but break down into the constituent chlorides. In the light of these facts it is impossible to conceive of sufficient double chloride existing in the solutions, to give them a pure blue color in the presence of the red cobalt chloride, even if a blue double chloride were formed.

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[1] J. Chim. Phys., **3**, 455 (1905);

[2] Z. physik. Chem., **49**, 385 (1904).

[3] THIS JOURNAL, **22**, 5 (1899).

[4] *Ibid.*, **22**, 110 (1899).

Again, the same reaction can be effected by adding concentrated hydrochloric acid to a concentrated solution of cobalt chloride, while no amount of the dilute acid will change the solution of the cobalt salt to a blue color. This cannot be due to the formation of a double compound with the hydrochloric acid, for the reasons already given for the salts.

The above color change of the solution of cobalt chloride from red to blue can also be effected by phosphorus pentoxide. When this dissolves an acid is formed, but the acid is so weak, relative to hydrochloric acid, that the amount of hydrochloric acid set free would be far less than in an ordinarily dilute solution of hydrochloric acid. The color change is effected by the phosphorus pentoxide, but not by dilute hydrochloric acid.

Taking into account the above and many other facts bearing upon the problem, it seems that any attempt to account for these color changes on the basis of the formation of double compounds must be regarded as untenable.

We have here, then, a well-defined example of hydration taking place in solution. In the case of crystallized calcium chloride, the change in color of the cobalt chloride demonstrates that the calcium chloride can and does combine with more water in solution than it can bring with it out of solution, as water of crystallization, which is the point to be proved.

If, to any of the cobalt solutions mentioned above, water be added, the blue color immediately disappears and the characteristic red color of the cobalt salt again makes its appearance. This is, of course, exactly in conformity with our conception that these experiments illustrate dehydration even in aqueous solutions.

Color reactions similar to the above can be effected with cupric bromide. When salts with large hydrating power are added to dilute solutions of cupric bromide, which are blue, a part of the water is removed from the cupric salt and the blue color gives way to the greenish, or greenish-brown, that is characteristic of concentrated, or only partially hydrated solutions of cupric bromide.

These reactions will not be referred to in any further detail in this connection, since they are now being studied quantitatively by means of the spectroscope.

The Effect of Temperature on Water of Crystallization, as Bearing on the Theory of Hydrates in Solution.

Another line of evidence, which seems to us to have some bearing, at least indirectly, on the question as to whether there is combination between the solvent and dissolved substances is the following: If dissolved substances combine with the solvent, we know that the resulting compounds are unstable, especially at elevated temperatures. That this is the case is shown by the fact that most of the water can readily be driven off from solutions of salts at the boiling-points of these solutions. Indeed, in most cases, practically all the water can be thus removed, except that which is held in combination by the salt at the temperature in question, as water of crystallization. We have already shown that salts which crystallize with water of crystallization can combine, when in solution, at ordinary temperatures, with a much larger amount of water than they can bring with them out of solution, when they crystallize. These hydrates are, then, more stable the lower the temperature and, in terms of our hydrate theory, we should expect that *a salt would be able to bring with it out of solution more water, as water of crystallization, the lower the temperature at which the crystals were formed.*

We were surprised, on examining the literature, to find how large an amount of evidence was available, bearing on this point. A good many cases are well known, but we found on record an unexpectedly large number of salts that have already been shown to crystallize with varying amounts of water, depending upon the temperature at which the crystals were formed. A few examples are given to bring out the general relation, that *the number of molecules of water of crystal-*

lization is greater the lower the temperature at which the salt is crystallized.

Salt.	Water of crystallization.	Temperature of crystallization.
LiCl	$2H_2O$	12°.5
"	$3H_2O$	—15°
LiBr	H_2O	
"	$2H_2O$	Not stable above 4°
"	$3H_2O$	—40°
$LiNO_3$	Anhydrous	15°
"	$5H_2O$	Below 10°
NaBr	Anhydrous	Hot, concentrated solution
"	$2H_2O$	Ordinary temperatures
NaI	Anhydrous	Hot, concentrated solution
"	$2H_2O$	Ordinary temperatures
Na_2CO_3	$7H_2O$	Warm, saturated solution
"	$10H_2O$	Ordinary temperatures
$CaCl_2$	H_2O	As the temperature of crystallization is lower and lower
"	$2H_2O$	
"	$4H_2O$	
"	$6H_2O$	
$Sr(NO_3)_2$	Anhydrous	Above 16°.8
"	$4H_2O$	Below 16°.8
$MgCl_2$	$6H_2O$	Elevated temperatures
"	$8H_2O$	Above 20°
"	$10H_2O$	20°
"	$12H_2O$	—10° to —12°
$MgBr_2$	$4H_2O$	11°.5 to 12°.5
"	$6H_2O$	
"	$10H_2O$	—16°
$Mg(NO_3)_2$	$2H_2O$	Elevated temperatures
"	$6H_2O$	18°
"	$9H_2O$	—17°
$ZnCl_2$	H_2O	Elevated temperatures
"	$2H_2O$	
"	$3H_2O$	—21°
$ZnBr_2$	Anhydrous	35°
"	$2H_2O$	—8°
"	$3H_2O$	—15°
$Zn(NO_3)_2$	$3H_2O$	36°

Salt.	Water of crystallization.	Temperature of crystallization.
$Zn(NO_3)_2$	$6H_2O$	From concentrated solution
"	$9H_2O$	—18°
$Cd(NO_3)_2$	$4H_2O$	Ordinary temperatures
"	$9H_2O$	10° to —16°
$CdSO_4$	H_2O	103° to 104°
"	$7H_2O$	—20°
"	$9H_2O$	Very low temperatures
$MnCl_2$	$2H_2O$	20°
"	$4H_2O$	15°
"	$6H_2O$	—21°
"	$11H_2O$	—21° to —37°
"	$12H_2O$	—48°
MnI_2	$4H_2O$	0° to —2°.7
"	$6H_2O$	—5°
"	$9H_2O$	—20°
$MnSO_4$	$3H_2O$	25° to 31°, as a crust
"	$4H_2O$	25° to 31°
"	$5H_2O$	15° to 20°
"	$7H_2O$	0° or below 6°
$Ni(NO_3)_2$	$3H_2O$	58° and above
"	$6H_2O$	—16°
"	$9H_2O$	—27°
$Co(NO_3)_2$	$3H_2O$	56° to 91°
"	$6H_2O$	—22° to 56°
"	$9H_2O$	—29° to —22°
$Cu(NO_3)_2$	$3H_2O$	At ordinary temperatures
"	$6H_2O$	About 0° to —10°
"	$9H_2O$	—20° to —24°
$AlCl_3$	$6H_2O$	2° to 20°
"	$9H_2O$	—8° to 2°
$AlBr_3$	$9H_2O$	Ordinary temperatures
"	$15H_2O$	—10° to —18°
AlI_3	$6H_2O$	Ordinary temperatures
"	$15H_2O$	—18°
$Fe(NO_3)_2$	$6H_2O$	—9°
"	$9H_2O$	—27°
$FeCl_3$	Anhydrous	80° and above
"	$2H_2O$	60° to 80

Salt.	Water of crystallization.	Temperature of crystallization.
$FeCl_3$	$2\frac{1}{2}H_2O$	40° to 60°
"	$3\frac{1}{2}H_2O$	20°
"	$6H_2O$	20° to —16°

While there is a much larger number of cases on record where water of crystallization varies with the temperature, in many of them the temperatures at which the different amounts of water of crystallization were obtained are either not given at all, or are given only approximately. Such cases, in their present state, are of comparatively little value as bearing on the problem under discussion.

The examples given above suffice to show the general nature of the relation between water of crystallization and the temperature at which the salt was crystallized. Work is now in progress on this point and we hope to find even a larger number of instances where temperature affects water of crystallization and, if possible, to establish even more marked effects of temperature on the amount of water with which the salt crystallizes.

It might be concluded that these facts are at variance with the relation, pointed out by Jones and Getman,[1] between water of crystallization and lowering of freezing-point. This is not the case because the amounts of water of crystallization, as taken by Jones and Getman, are the quantities with which the salts ordinarily crystallize, *i. e.*, under as nearly comparable conditions of temperature as possible. These facts, then, have no direct bearing on the above relation, which is regarded as strong evidence in support of our hydrate conception.

Aim of the Present Investigation.

The aim of the present investigation is to determine, as closely as possible, the composition of the hydrates formed by a number of familiar salts, acids and bases, at different concentrations. The methods employed are similar to those used in the earlier parts of this work and especially in the investigation, an account of which has recently appeared.[1]

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[1] THIS JOURNAL, 31, 344. Z. physik. Chem., 49, 433 (1904). J. Chim. Phys., 3, 455 (1905).

The *freezing-point lowerings* produced by the various substances, over as wide range of dilution as was practicable, were measured. The more concentrated solutions were frozen by means of a mixture of solid carbon dioxide and alcohol, the freezing-temperatures being determined by means of alcohol thermometers. These temperatures could not be measured more closely than 0°.5, and we are not certain of our measurements for the very low temperatures to within 1°. For the more dilute solutions, Beckmann thermometers, covering a range of 5°, 12° and 25°, respectively, were used. When the more concentrated solutions were frozen they were removed from the bath of solid carbon dioxide and alcohol as soon as ice began to separate, in order that they might not be surrounded by the very cold freezing-mixture while temperature equilibrium was being established. The proper correction was introduced, in every instance, for the increase in concentration due to the separation of the ice. It was always a perfectly simple matter to ascertain when pure ice separated from the solution, or when some of the dissolved substance was deposited. This could usually be determined by the grit or sand-like character of the solid that separated, which was easily detected by rubbing the stirrer up and down in the freezing-tube. In all cases it could be detected by the behavior of the thermometer, as more and more of the solid was allowed to separate. When the cryohydric point was once reached the thermometer remained stationary as more and more of the solid separated. Otherwise, the thermometer would fall as more and more pure ice separated and increased the concentration of the solution. That solid solutions were formed seems highly improbable.

The *conductivities* of the solution were measured at 0°, in order to be able to ascertain, as nearly as possible, the dissociation at that temperature. The value of $\mu\infty$ was determined directly, whenever it was practicable to do so, simply by increasing the dilution of the solution until the molecular conductivity reached a maximum, constant value. In other cases the value of $\mu\infty$ was obtained from the velocities of the ions in question and Kohlrausch's law ; $\mu\infty = a + c$.

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[1] THIS JOURNAL, 33, 534 (1905).

It is well known that the conductivity method is not an accurate measure of dissociation in concentrated solutions. It is, however, an approximate method of measuring such dissociations and is the best we can do at present. All that can be said is, that it probably gives values of the right order of magnitude.

Since concentrated solutions contain, in a liter of solution, less than 1000 grams of water, it is necessary to determine the *specific gravities* of all such solutions, in order to correct the freezing-point lowering actually observed, for the difference between the amount of water really present in the solution and 1000 grams of water. The observed freezing-point lowering, thus corrected, can then be compared directly with the freezing-point constant of water, increased in terms of the percentage dissociation of the solution in question.

Calculation of the Approximate Composition of the Hydrates.

Given the above data, the calculation of the amount of water in combination with the dissolved substance is simple. The observed molecular lowering is corrected for the difference between 1000 grams and the amount of water actually present in 1 liter of the solution. This gives the true molecular lowering, produced by the substance at the dilution in question, if there were 1000 grams of water present.

The calculated molecular lowering can now be compared directly with the corrected, observed molecular lowering. If there was no hydration these two values would be equal. The magnitude of the hydration is obtained as follows :

The calculated molecular lowering is divided by the corrected molecular lowering found. This ratio, multiplied by 1000, gives the amount of water present playing the rôle of solvent, if the quantity of the substance present was dissolved in 1000 grams of water.

The difference between this amount of water and 1000 grams, is the quantity that is in combination with the dissolved substance, under the conditions that obtain in the solution in question.

For a number of reasons everything is referred to 1000 grams of the solvent. The theoretical freezing-point constant is calculated for 1000 grams of the solvent and, by calculating the depression found for the same amount of the solvent, the two sets of results are comparable. Further, by referring everything to a constant amount of the solvent, the various results can be compared directly with one another.

If we know the number of grams of water that have combined with the dissolved substance, the number of gram-molecules of water that have entered into combination is obtained by dividing the above value by 18. If we divide this value by the concentration in terms of normal, we obtain the number of molecules of water in combination with 1 molecule of the dissolved substance, when the amount of substance present in a liter of the solution is dissolved in 1000 grams of water.

The Results.

In order to calculate the composition of the hydrates formed by any given substance, at different dilutions, it is necessary to have the following values:

The lowering of the freezing-point produced by the dissolved substance.

The conductivity of the solution as an approximate measure of its dissociation.

The specific gravities of the solutions, in order to calculate the difference between 1000 grams of water and the amount contained in a liter of the solution.

Some of the above data were already available for the following substances. However, in a few cases a part of the data had been secured and this we have supplemented wherever necessary.

The compositions of the hydrates, formed by the following substances, are calculated as closely as seems to be possible: Lithium iodide, sodium bromide, strontium nitrate, barium iodide, cadmium nitrate, chromium chloride, potassium ferrocyanide, potassium ferricyanide, sodium chromate, sodium dichromate, disodium phosphate, ammonium cupric chloride, potassium cupric chloride, ammonium sodium acid phosphate, hydrochloric acid, hydrobromic acid, nitric acid, phosphoric acid, chromic acid, sodium hydroxide, potassium hydroxide and ammonium hydroxide.

In the various tables of data the symbols have the following significance:

In the tables of freezing-point measurements, m is the concentration, in terms of gram-molecules per liter; Δ the observed freezing-point lowering, corrected for the separation of ice and $\frac{\Delta}{m}$ the molecular lowering of the freezing-point.

In the conductivity tables the symbols have the usual significance, v is the volume of the solution, or the number of liters that contain a gram-molecular weight of the electrolyte; α is the approximate dissociation.

In the specific gravity tables m is the concentration; $W_{\text{Sol.}}$ the weight of 25 cc. of the solution; W_{Salt} the weight of the salt contained in 25 cc. of the solution; and W_{H_2O} the weight of water contained in 25 cc. of the solution. The percentage correction is the correction that must be applied to the freezing-point lowering, in order to refer it to 1000 grams of solvent, instead of the amount of water that is present in a liter of the solution in question.

The symbols in the hydrate tables have the following significance; m is the concentration in terms of gram-molecules per liter; α the approximate dissociation of the solution; L the theoretical molecular lowering of the freezing-point referred to 1000 grams of the solvent; $\frac{\Delta}{m}$ the molecular lowering found experimentally; L′ the molecular lowering; m' the number of gram-molecules of water in combination, both being referred to 100 grams of water; H the number of molecules of water in combination with 1 molecule of the salt, at the concentration in question, if a liter of the solution, at that concentration, contained 1000 grams of water.

In order to ascertain the number of molecules of water actually in combination with 1 molecule of the dissolved substance, at the concentration given, it is only necessary to divide the value of m' for that concentration, by the concentration expressed in terms of a gram-molecular weight in 1000 grams of the solvent. The difference between the values of H found by these two methods is generally quite negligible, being smaller than experimental errors. It becomes appreciable only when the "correction" per cent is large, *i. e.*, in very concentrated solutions.

Lithium Iodide.

The freezing-point, conductivity and specific gravity measurements were made by Jones and Getman.[1] We find a somewhat higher value for $\mu\infty$, which makes the dissociations lower.

The total amount of water in combination with the salt increases with the concentration of the solution, in a fairly regular manner, as is shown in the curve, Fig. I. The number of molecules of water in combination with 1 molecule of the salt, increases from the most concentrated to the most dilute solution.

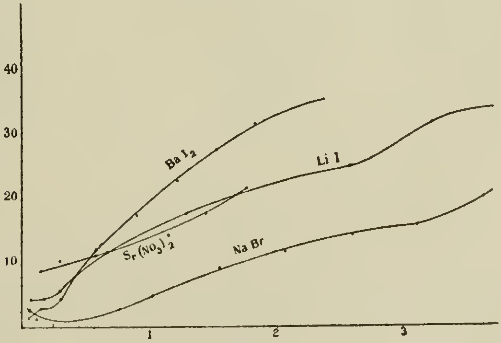

Fig. I.

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[1] Z. physik. Chem., **49**, 391 (1904).

Table I.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.080	0°.296	3.70
0.161	0°.588	3.65
0.322	1°.218	3.79
0.645	2°.700	4.19
1.290	6°.140	4.75
2.580	16°.200	6.28
3.22	25°.000	7.76
5.16	59°.000	11.43

Table II.—Conductivity Measurements.

$\mu\infty$ 0° = 62.0.

v.	μ_v 0°.	α.
0.18	23.63	39.1
0.31	34.27	55.4
0.38	42.00	67.7
0.77	42.50	68.5
1.55	46.44	74.9
3.10	49.50	79.8
6.21	49.65	80.1
12.50	51.40	82.9

Table III.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.080	25.1427	0.2678	24.8749	0.50
0.161	25.3482	0.5389	24.8093	0.76
0.322	25.7813	1.0779	24.7034	1.19
0.645	26.6130	2.1341	24.4789	2.08
1.29	28.1726	4.3183	23.8533	4.59
2.58	31.2754	8.6365	22.5389	9.84
3.22	32.9292	10.7789	22.1503	11.40
5.16	37.5566	17.2731	20.2835	18.87

Table IV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$	L′.	m'.	H.
0.080	0.829	3.40	3.70	3.68	4.23	52.8
0.161	0.801	3.35	3.65	3.63	4.29	26.6
0.322	0.798	3.34	3.79	3.75	6.07	18.5
0.645	0.749	3.25	4.19	4.10	11.52	17.8
1.29	0.685	3.13	4.75	4.54	17.25	13.4
2.58	0.677	3.12	6.28	5.67	24.99	9.7
3.22	0.554	2.89	7.76	6.88	32.22	10.0
5.60	0.391	2.59	11.43	9.27	40.03	7.15

Sodium Bromide.

The freezing-point measurements, the conductivities and the specific gravities were worked out by Jones and Getman.[1]

We think the value 64.48 a little nearer the true value of $\mu\infty$ than the value 60.85, used by Jones and Getman. This alters somewhat the value of the dissociation and, consequently, the composition of the hydrates, as calculated.

The amount of water in combination is plotted against the concentration in the curve, Fig. I.

Table V.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.07	0°.245	3.77
0.13	0°.462	3.55
0.26	0°.907	3.49
0.52	1°.842	3.54
1.03	3°.815	3.70
1.55	6°.200	4.00
2.07	8°.610	4.16
2.59	11°.350	4.36
3.10	14°.000	4.52
3.62	18°.000	4.98

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[1] Z. physik. Chem., **49**, 394 (1904).

Table VI.—Conductivity Measurements.

$\mu\infty$ 0° = 64.48.

v.	μ_v 0°.	α.
0.27	34.52	53.5
0.32	37.78	58.6
0.38	40.26	62.4
0.48	43.39	67.3
0.64	46.07	71.4
0.97	48.31	74.9
1.92	51.12	79.3
3.85	54.00	83.7
7.69	55.38	85.8
15.38	59.02	91.5

Table VII.—Specific Gravity Measurements.

m.	W Sol.	W Salt.	W_{H_2O}.	Correction. Per cent.
0.07	25.1144	0.1802	24.9342	0.26
0.13	25.2390	0.3348	24.9042	0.38
0.26	25.4923	0.6695	24.8228	0.71
0.52	25.9538	1.3390	24.6128	1.54
1.03	27.0571	2.6780	24.3791	2.48
1.55	28.0156	3.9912	24.0244	3.90
2.07	29.0257	5.3302	23.6955	5.22
2.59	29.9884	6.6942	23.2942	6.82
3.10	30.9610	7.9825	22.9788	8.09
3.62	31.9614	9.3215	22.6399	9.44

Table VIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.	m'.	H.
0.07	0.915	3.56	3.77	3.76	2.96	42.2
0.13	0.858	3.46	3.55	3.54	1.26	9.66
0.26	0.837	3.42	3.49	3.47	0.43	1.65
0.52	0.793	3.32	3.54	3.49	2.70	5.20
1.03	0.749	3.25	3.70	3.61	5.54	5.38
1.55	0.714	3.19	4.00	3.84	9.40	6.07
2.07	0.673	3.11	4.16	3.94	11.70	5.65
2.59	0.624	3.02	4.36	4.06	14.23	5.49
3.10	0.586	2.95	4.52	4.15	16.06	5.18
3.62	0.535	2.86	4.98	4.51	20.33	5.62

Strontium Nitrate.

A solution of strontium nitrate was standardized and a new set of freezing-point measurements made. The total amount of water in combination, increases regularly with the concentration and the number of molecules of water, in combination with 1 molecule of the salt, increases from the most concentrated to the most dilute solution.

Table IX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.145	0°.68	4.70
0.290	1°.35	4.65
0.580	2°.44	4.20
1.161	4°.70	4.05
1.451	5°.85	4.03
1.741	7°.13	4.09
1.8137	7°.50	4.13

Table X.—Conductivity Measurements.

$\mu\infty\ 0° = 152.7$.

v.	μ_v 0°.	α.
0.57	30.00	19.6
0.68	34.00	22.3
0.86	40.60	26.6
1.72	56.70	37.1
3.45	76.60	50.2
6.89	80.90	53.0
13.88	90.86	59.5

Table XI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction. Per cent.
0.145	25.6525	0.7676	24.8849	0.46
0.290	26.2575	1.5353	24.7222	1.11
0.580	27.5152	3.0705	24.4447	2.22
1.161	30.7750	6.1463	24.6287	1.48
1.451	32.5280	7.6816	24.8464	0.61
1.741	34.4900	9.2168	25.2732	—1.09
1.8137	35.0225	9.6017	25.4208	—1.68

Table XII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.	m'.	H.
0.145	0.530	3.93	4.70	4.68	8.91	61.4
0.290	0.502	3.73	4.65	4.60	10.51	36.2
0.580	0.371	3.24	4.20	4.11	11.73	20.2
1.161	0.266	2.95	4.05	3.99	14.48	12.5
1.451	0.223	2.69	4.03	4.01	18.29	12.6
1.741	0.196	2.59	4.09	4.13	20.72	11.3

Barium Iodide.

The freezing-points, conductivities and specific gravities are taken from the work of Jones and Getman.[1] The value 143 seems a little nearer to the true value of $\mu\infty$ at 0° than the value previously used. This changes, slightly, the values for the dissociation. While the total amount of combined water increases with the concentration (see curve, Fig. I.), the number of molecules of water combined with 1 molecule of the dissolved substance is nearly constant for all the dilutions studied.

Table XIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.076	$0^\circ.374$	4.92
0.153	$0^\circ.764$	5.00
0.306	$1^\circ.584$	5.17
0.612	$3^\circ.720$	6.08
0.917	$6^\circ.130$	6.69
1.222	$9^\circ.220$	7.54
1.528	$13^\circ.250$	8.67
1.834	$17^\circ.500$	9.54
2.139	$24^\circ.000$	11.22

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[1] Z. physik. Chem., **49**, 408 (1904).

Table XIV.—Conductivity Measurements.

$\mu_\infty\ 0° = 143$.

v.	μ_v 0°.	α.
0.32	39.60	27.7
0.37	50.10	35.0
0.47	64.40	45.0
0.54	73.10	51.1
0.65	79.34	55.5
0.82	87.36	61.1
1.09	92.66	64.8
1.61	101.52	71.0
3.26	105.72	74.9
6.53	108.50	75.9
13.16	112.45	78.6

Table XV.—Specific Gravity Measurements.

m.	$W_{\text{Sol.}}$	$W_{\text{Salt.}}$	W_{H_2O}.	Correction. Per cent.
0.076	25.6084	0.6843	24.9241	0.30
0.153	26.2575	1.4662	24.7913	0.83
0.306	27.4888	2.9325	24.5563	1.77
0.612	30.0284	5.9628	24.0656	3.74
0.917	32.5060	8.9930	23.513	5.95
1.222	35.0114	11.9255	23.0859	7.46
1.528	37.5227	14.9557	22.5670	9.73
1.834	40.0067	17.8882	22.1185	11.53
2.139	42.4761	20.9185	21.5576	13.77

Table XVI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.076	0.786	4.78	4.92	4.91	1.47	19.3
0.153	0.759	4.68	5.00	4.96	3.14	20.5
0.306	0.749	4.65	5.17	5.08	4.70	15.4
0.612	0.710	4.54	6.08	5.86	12.51	20.4
0.917	0.648	4.27	6.69	6.29	17.84	19.5
1.222	0.611	4.13	7.54	6.98	22.70	18.1
1.528	0.555	3.92	8.67	7.83	27.74	18.2
1.834	0.511	3.76	9.54	8.44	31.92	17.4
2.139	0.450	3.53	11.22	9.67	35.28	16.5

Cadmium Nitrate.

According to the earlier work, cadmium nitrate gave somewhat too great lowering of the freezing-point, for a salt with 4 molecules of water of crystallization. Having repeated the work with this substance, we find somewhat smaller lowerings, the difference probably being due to some error in the original work, possibly in the standardization of the solution. We find that the salt gives just about the lowering that we should expect from its water of crystallization.

The results for the amount of combined water are plotted in Fig. II. The number of molecules of water combined with 1 molecule of the dissolved substance increases with the dilution of the solution.

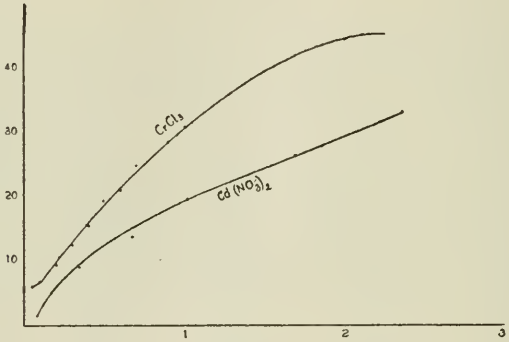

Fig. II.

Table XVII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.0845	0°.41	4.85
0.1691	0°.85	5.03
0.3382	1°.73	5.12
0.6764	3°.50	5.18
1.0146	5°.73	5.65
1.6910	10°.58	6.38
2.3674	17°.00	7.18

Table XVIII.—Conductivity Measurements.

μ_∞ 0° = 116.5.

v.	μ_v 0°.	α.
0.42	23.47	20.1
0.59	34.27	29.4
0.98	50.22	43.1
1.48	59.00	50.7
2.95	73.42	63.0
5.91	83.55	71.7
11.83	87.17	74.8

Table XIX.—Specific Gravity Determinations.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.0845	25.3835	0.4995	24.8840	0.46
0.1691	25.8521	0.9990	24.8531	0.59
0.3382	26.6653	1.9980	24.6673	1.33
0.6764	28.1045	3.9960	24.1085	3.57
1.0146	29.7375	5.9940	23.7435	5.03
1.6910	32.7386	9.9900	22.7486	9.01
2.3674	35.5865	13.9860	21.6005	13.60

Table XX.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.0845	0.748	4.64	4.82	4.80	1.85	21.9
0.1691	0.717	4.53	5.03	5.00	5.22	30.9
0.3382	0.630	4.20	5.12	5.05	9.36	27.7
0.6764	0.507	3.75	5.18	5.00	13.89	20.5
1.0146	0.431	3.46	5.65	5.37	19.76	19.5
1.6910	0.294	2.94	6.38	5.81	26.49	15.7
2.3674	0.201	2.51	7.18	6.20	33.06	13.9

Chromium Chloride.

The chloride of chromium is an interesting substance to study in the present connection, on account of it being a quarternary electrolyte, having 6 molecules of water of crystallization and being very soluble in water.

The results are just what would have been expected from our earlier work with similar compounds. The total amount of water combined with the salt is large and increases from the most dilute to the most concentrated solution (see Fig. II.).

The number of molecules of water combined with 1 molecule of the dissolved substance is, as would be expected, large, and increases from the most concentrated to the most dilute solution.

Table XXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.268	5.36
0.1	0°.510	5.10
0.2	1°.030	5.15
0.3	1°.570	5.23
0.4	2°.160	5.45
0.5	2°.910	5.82
0.6	3°.610	6.016
0.7	4°.55	6.50
0.9	6°.30	7.00
1.0	7°.46	7.46
1.5	15°.00	10.00
2.0	27°.00	13.50
2.25	33°.00	14.67

Table XXII.—Conductivity Measurements.

$\mu\infty$ 0° = 190.

v.	μ_v 0°.	α.
0.40	14.46	7.61
0.44	18.31	9.64
0.50	22.60	11.63
0.67	32.19	16.94
1.00	45.40	23.90
1.11	48.62	25.60
1.43	55.47	29.20
1.67	59.27	31.20
2.00	63.12	33.22
2.50	68.11	35.85
3.33	72.37	38.10
5.00	79.70	41.95
10.00	89.14	46.92
20.00	100.2	52.73

Table XXIII.—Specific Gravity Measurements.

m.	$W_{sol.}$	$W_{salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.2479	0.1981	25.0498	0.20
0.1	25.3552	0.3961	24.9591	0.16
0.2	25.6458	0.7923	24.8535	0.59
0.3	25.9221	1.1884	24.7337	1.06
0.4	26.2676	1.5845	24.6831	1.27
0.5	26.5693	1.9806	24.5887	1.64
0.6	26.9335	2.3768	24.5567	1.77
0.7	27.2232	2.7729	24.4503	2.20
0.9	27.7939	3.5651	24.2288	3.09
1.0	28.0684	3.9613	24.1071	3.57
1.5	29.5153	5.9419	23.5734	5.71
2.0	30.9932	7.9225	23.0207	7.92
2.25	31.5784	8.9128	22.6656	9.34

Table XXIV.—Hydrates.

m.	*α.*	L.	$\frac{\Delta}{m}$.	L′.	*m′.*	H.
0.05	0.527	4.80	5.36	5.37	5.90	117.94
0.1	0.469	4.48	5.10	5.09	6.66	66.58
0.2	0.420	4.20	5.15	5.12	9.98	49.91
0.3	0.381	3.99	5.23	5.18	12.76	42.54
0.4	0.359	3.86	5.45	5.38	15.70	39.24
0.5	0.332	3.71	5.82	5.73	19.58	39.17
0.6	0.312	3.60	6.01	5.91	21.16	35.27
0.7	0.292	3.49	6.50	6.36	25.07	35.81
0.9	0.256	3.29	7.00	6.78	28.60	31.78
1.0	0.239	3.19	7.46	7.19	30.91	30.91
1.5	0.169	2.80	10.00	9.43	39.05	26.04
2.0	0.116	2.52	13.50	12.42	44.28	22.14
2.25	0.096	2.40	14.67	13.30	45.53	20.24

Potassium Ferrocyanide.

This salt was chosen, on account of the statement in the literature that it dissociates thus, $\overset{+}{\mathrm{K}},\overset{+}{\mathrm{K}},\overset{+}{\mathrm{K}},\overset{+}{\mathrm{K}},(\overline{\overline{\overline{\overline{\mathrm{Fe(CN)}}}}})_6$, yielding 5 ions. We shall see, later, that this is doubtful. The molecular lowerings of the freezing-point that were produced were small ; indeed, so small that there was no evidence of any appreciable hydration in the solutions. We then took up the problem as to whether there is *any appreciable time factor in the conductivity* of solutions of potassium ferrocyanide. The following solutions of the salt were prepared and their conductivities determined at 25°.

v.	μ_v 25°.
40	369.4
80	405.5
160	447.8
320	496.2
400	507.4

After making these measurements the solutions were allowed to remain in the thermostat-bath, for 30 minutes and their conductivities redetermined. No appreciable change was detected. The conductivities were measured again, after the solutions had stood for 4 hours and still no change of any moment manifested itself. The same result was obtained after the solutions had stood for more than 24 hours.

A change in the conductivity might have occurred before the first conductivity measurements were made. To test this, some of the salt was weighed in the dry conductivity cup and a known quantity of water, which had already been brought to the temperature of the bath, added. In a very few minutes the first conductivity reading was made. The conductivity did not change an appreciable amount on allowing the solutions to stand.

It was then decided to determine whether there is any *change in the freezing-point lowering with time.* Fresh solutions were prepared and their freezing-points determined immediately. The solutions were then allowed to stand and their freezing-points determined from time to time. No change could be detected.

The *value of* $\mu\infty$ was then determined for potassium ferroyanide, at 25°, with the following result :

v.	μ_v 25°.
640	530
1280	557
2560	580
5120	575

The value of $\mu\infty$ seems to have been reached at a dilution of from 3000–5000 liters.

Dissociation of Potassium Ferrocyanide.

The magnitude of this value throws some light on the question as to how potassium ferrocyanide dissociates. It is almost exactly the value that would have been obtained if potassium ferrocyanide dissociated thus :

$$K_4Fe(CN)_6 = \overset{+}{K}, \overset{+}{K}, \overset{+}{K}, \overset{-}{CN}, \overset{-}{CN}, \overset{-}{CN}, \overset{+}{K}, Fe(\overset{-}{CN})_3.$$

Table XXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.580	5.80
0.2	1°.05	5.25
0.3	1°.45	4.83
0.4	1°.78	4.45

Table XXVI.—Conductivity Measurements.

v.	μ_v 0°.
2.00	154.1
2.50	156.0
3.33	158.4
5.00	163.4
10.00	171.8

Table XXVII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	25.6794	0.9221	24.7573	0.97
0.2	26.2775	1.8442	24.4333	2.27
0.3	26.8744	2.7663	24.1081	3.57
0.4	27.5021	3.6884	23.8137	4.75
0.5	28.0540	4.6105	23.4435	6.23

Potassium Ferricyanide.

The freezing-point lowerings were small and, therefore, the salt showed no hydration.

Dissociation of Potassium Ferricyanide.

Light could be thrown on the *way in which potassium ferricyanide dissociated,* by comparing the conductivity of this salt with that of potassium ferrocyanide at the same dilutions. The differences were just about what would be expected, if the solutions of the ferrocyanide contained one more molecule of potassium cyanide than those of the ferricyanide. From this we conclude that potassium ferricyanide dissociates thus:

$$K_3Fe(CN)_6 = \overset{+}{K},\overset{-}{CN},\overset{+}{K},\overset{-}{CN},\overset{+}{K},Fe(\overset{-}{CN})_4.$$

This is also in accord with the value found for $\mu\infty$ for this substance.

Table XXVIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	$0^\circ.30$	6.00
0.1	$0^\circ.56$	5.60
0.2	$1^\circ.086$	5.43
0.3	$1^\circ.57$	5.23
0.4	$2^\circ.05$	5.12

Table XXIX.—Conductivity Measurements.

v.	μ_v 0°.
2.50	146.1
3.33	149.2
5.00	154.3
10.00	162.8
20.00	172.4

Table XXX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.2408	0.4121	24.8287	0.69
0.1	25.5037	0.8242	24.6795	1.28
0.2	25.9084	1.6483	24.2601	2.96
0.3	26.3277	2.4725	23.8552	4.58
0.4	26.8154	3.2966	23.5188	5.93

Sodium Chromate.

Sodium chromate, being fairly soluble, was brought within the scope of this work. It was not expected that the chromates would give normal results, but, like the sulphates, would behave abnormally. It is quite possible that the chromate is somewhat polymerized and that this is offset by the hydration. The results would indicate the power to combine with a small amount of water in the more concentrated solutions.

Solutions of greater concentrations could not be used, on account of the salt separating out at the low temperatures.

Table XXXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.450	4.50
0.2	0°.850	4.25
0.3	1°.230	4.10
0.4	1°.604	4.01
0.5	1°.960	3.92
0.6	2°.345	3.90
0.8	3°.063	3.83
1.0	3°.800	3.80

Table XXXII.—Conductivity Measurements.

v.	μ_v 0°.	*α.*
1.00	53.95	45.0
1.25	57.59	48.0
2.00	69.0	57.5
2.50	72.5	60.4
3.33	76.0	63.5
5.00	80.0	66.7
10.00	89.4	74.5
20.00	97.0	80.8

Table XXXIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.1875	0.2028	24.9847	0.06
0.10	25.3800	0.4055	24.9745	0.10
0.20	25.7175	0.8110	24.9065	0.37
0.30	26.0600	1.2165	24.8435	0.62
0.40	26.4025	1.6220	24.7805	0.88
0.50	26.7325	2.0275	24.7050	1.18
0.60	27.0850	2.4330	24.6520	1.39
0.80	27.7500	3.2440	24.5060	1.98
1.00	28.4150	4.0550	24.3600	2.56

Table XXXIV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	*m*′.	H.
0.05	0.808	4.86	4.86	4.86	..	..
0.10	0.745	4.63	4.50	4.50	..	..
0.20	0.667	4.34	4.25	4.23	..	..
0.30	0.635	4.22	4.10	4.07	..	..
0.40	0.604	4.11	4.01	3.97	..	..
0.50	0.575	4.00	3.92	3.87	..	..
0.60	0.543	3.88	3.91	3.86	..	..
0.80	0.480	3.64	3.83	3.75	1.67	2.1
1.00	0.450	3.53	3.80	3.70	2.55	2.55

Sodium Dichromate.

Sodium dichromate was quite readily soluble in water at ordinary temperatures, but, at the freezing-points the solubility was greatly diminished. We could, therefore, work only with fairly dilute solutions.

The results show very considerable hydrating power on the part of sodium dichromate, which increases with fair regularity from the most concentrated to the most dilute solution.

The results for the dichromate cannot, of course, be compared with those for the chromate, as the two compounds are salts of such different acids. The dichromate behaves about as would be expected.

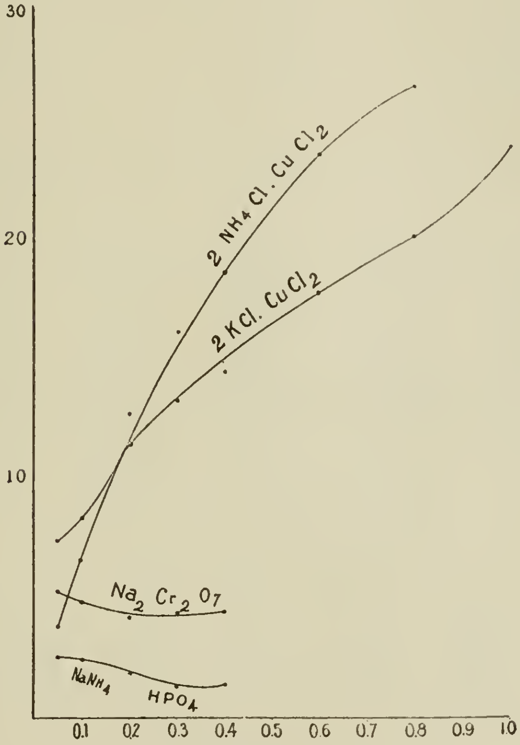

Fig. III.

Table XXXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.490	4.90
0.2	0°.946	4.73
0.3	1°.400	4.66
0.4	1°.872	4.68

Table XXXVI.—Conductivity Measurements.

$\mu_\infty\ 0^\circ = 125.5.$

v.	$\mu_v\ 0^\circ$.	α.
2.50	81.5	65.0
3.33	85.7	68.2
5.00	89.0	71.0
10.00	95.0	75.7
20.00	100.8	80.5

Table XXXVII.—Specific Gravity Measurements.

m.	$W_{\text{Sol.}}$	$W_{\text{Salt.}}$	W_{H_2O}.	Correction. Per cent.
0.05	25.2375	0.3304	24.9071	0.37
0.10	25.4750	0.6607	24.8143	0.74
0.20	25.9425	1.3215	24.6210	1.52
0.30	26.4200	1.9822	24.4378	2.25
0.40	26.8900	2.6430	24.2470	3.01
0.60	27.8050	3.9644	23.8406	4.64
0.80	28.7275	5.2860	23.4415	6.23
1.00	29.6225	6.6075	23.0150	7.94
1.25	30.7125	8.2594	22.4531	10.19

Table XXXVIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.10	0.757	4.68	4.90	4.86	2.05	20.5
0.20	0.710	4.50	4.73	4.66	1.94	9.7
0.30	0.682	4.40	4.66	4.56	1.94	6.5
0.40	0.650	4.28	4.68	4.54	3.16	7.9

Disodium Phosphate.

Disodium phosphate was an especially interesting salt to study, in the present connection, on account of the large amount of water with which it crystallizes. It crystallizes with more water (12 molecules) than any other salt thus far employed in the present connection. It is unfortunate that the salt has such slight solubility in water at the freezing-point of the solutions. We were not able to study solutions more concentrated than 0.1 N.

The results, however, show conclusively that disodium phosphate has greater power to combine with water than any other substance that we have investigated, which is of importance in connection with our relation between water of crystallization and lowering of freezing-point.

Table XXXIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.427	4.27
0.05	0°.237	4.74

Table XL.—Conductivity Measurements.

v.	μ_v 0°.	α.
10	62.8	34.9
20	70.6	39.2

Table XLI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.1	25.4325	0.3553	25.0772	—0.31
0.5	25.2580	0.1776	25.0806	0.32

Table XLII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.392	3.32	4.74	4.75	16.72	334.4
0.10	0.349	3.22	4.27	4.28	13.76	137.6

Ammonium Sodium Acid Phosphate.

The ammonium sodium acid phosphate crystallizes with 4 molecules of water and was, therefore, of interest from our standpoint. It combines with considerable water, especially in the dilute solutions, indeed, with just about the amount that we should expect from its water of crystallization.

The phosphates, then, fall in line with the general relation between water of crystallization and lowering of freezing-point.

Table XLIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.224	4.45
0.1	0°.420	4.20
0.2	0°.773	3.87
0.3	1°.088	3.63
0.4	1°.408	3.52

Table XLIV.—Conductivity Measurements.

μ_∞ 0° = 120.

v.	μ_v 0°.	α.
2.5	49.1	0.409
3.33	53.1	0.443
5.0	59.5	0.500
10.0	69.0	0.575
20.0	76.7	0.639

Table XLV.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.1425	0.1714	24.9711	0.12
0.1	25.2775	0.3428	24.9347	0.26
0.2	25.5500	0.6857	24.8643	0.54
0.3	25.7925	1.0285	24.7640	0.94
0.4	26.0575	1.3714	24.6861	1.26

Table XLVI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.	m'.	H.
0.05	0.639	4.24	4.45	4.45	2.61	52.2
0.10	0.575	4.00	4.20	4.19	2.50	25.0
0.20	0.500	3.72	3.87	3.85	1.88	9.4
0.30	0.443	3.51	3.63	3.60	1.39	4.6
0.40	0.409	3.38	3.52	3.48	1.55	3.9

Ammonium Cupric Chloride.

Having studied a large number of the salts of simple acids, we extended our work so as to include a few salts of complex acids. We selected the double chloride of ammonium and copper, since it could readily be obtained in a pure condition.

When the double chlorides dissolve in water they break down, for the most part, into the single salts, as has been shown by Jones and Knight.[1] The power to combine with water would, then, be essentially the power of the single salts to combine with it in the presence of one another.

Table XLVII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.600	12.00
0.1	1°.214	12.14
0.2	2°.515	12.57
0.3	3°.964	13.21
0.4	5°.500	13.75
0.6	8°.700	14.50
0.8	12°.00	15.00
1.0		

Table XLVIII.—Conductivity Measurements.

v.	μ_v 0°.	α.
1.00	130.4	43.6
1.25	146.1	48.9
1.66	162.9	54.5
2.50	187.4	62.7
3.33	197.6	66.1
5.00	205.6	68.7
10.00	235.1	78.5
20.00	248.6	83.2

Table XLIX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	W_{H_2O}.	Correction. Per cent.
0.05	25.1975	0.2919	24.9056	0.38
0.1	25.3875	0.5837	24.8038	0.78
0.2	25.7925	1.1674	24.6251	1.50
0.3	26.2075	1.7511	24.4564	2.17
0.4	26.5875	2.3348	24.2527	2.99
0.6	27.3200	3.5022	23.8178	4.73
0.8	28.0675	4.6696	23.3979	6.41

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[1] THIS JOURNAL, **22**, 110 (1899).

Table L.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.	m'.	H.
0.05	0.832	11.14	12.00	11.96	3.83	76.6
0.10	0.785	10.62	12.14	12.05	6.61	66.1
0.20	0.687	9.54	12.57	12.39	12.77	63.85
0.30	0.661	9.23	13.31	13.02	16.18	53.9
0.40	0.627	8.86	13.75	13.34	18.66	46.65
0.60	0.545	7.94	14.50	13.82	23.64	39.4
0.80	0.489	7.32	15.00?	14.04	26.59	33.23
1.00	0.436					

Potassium Cupric Chloride.

Another salt of a complex acid, which we could readily obtain in pure condition, was potassium cupric chloride. This, like the corresponding ammonium salt, breaks down in solution, into the two single chlorides. The total amount of water in combination increases very regularly from the most dilute to the most concentrated solution, and the number of molecules of water in combination with one of the salt, or the resulting ions, increases from the most concentrated to the most dilute solution.

Table LI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.623	12.46
0.1	1°.200	12.00
0.2	2°.425	12.12
0.3	3°.668	12.23
0.4	5°.00	12.50
0.6	7°.50	12.50
0.8	10°.00	12.50
1.0	13°.00	13.00

Table LII.—Conductivity Measurements.

v.	μ_v 0°.	α.
1.00	127.0	44.3
1.25	143.3	50.0
1.66	159.0	55.5
2.50	183.6	64.1
3.33	186.0	65.0
5.00	196.5	68.5
10.00	212.0	74.0
20.00	228.1	79.6

Table LIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Salt.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.2625	0.3546	24.9079	0.37
0.1	25.5225	0.7092	24.8133	0.75
0.2	26.0600	1.4184	24.6416	1.43
0.3	26.5825	2.1276	24.4549	2.18
0.4	27.1075	2.8368	24.2707	2.92
0.6	28.1175	4.2552	23.8613	4.55
0.8	29.1100	5.6736	23.4364	6.25
1.0	30.0875	7.0920	22.9955	8.02

Table LIV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.796	10.74	12.46	12.41	7.48	149.6
0.1	0.740	10.11	12.00	11.91	8.40	84.0
0.2	0.685	9.50	12.12	11.95	11.39	56.9
0.3	0.650	9.11	12.23	11.97	13.28	44.3
0.4	0.641	9.02	12.50	12.14	14.28	35.7
0.6	0.555	8.05	12.50	11.93	18.07	30.1
0.8	0.500	7.44	12.50	11.72	20.29	25.4
1.0	0.443	6.80	13.00	11.96	23.97	24.0

Hydrochloric Acid.

Having investigated a fairly large number of salts we then studied some of the more common acids and measured the freezing-point lowerings produced by solutions as concentrated as could be used with the thermometers at our disposal. Dilutions ranging from 6 N to 0.05 N were employed.

In very dilute solutions hydrochloric acid does not seem to have the power of combining with water. The amount of combined water increases with the concentration, from about 0.3 N to the most concentrated solution that was studied (see curve, Fig. IV.).

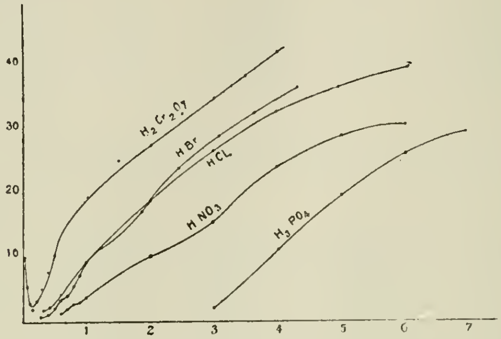

Fig. IV.

A possible explanation of the fact that, in dilute solutions, hydrochloric acid does not combine with water at all, is given at the end of this paper, under the general discussion.

Table LV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.174	3.59
0.1	0.355	3.55
0.2	0.712	3.56
0.3	1.080	3.60
0.4	1.442	3.60
0.5	1.832	3.66
0.6	2.250	3.75
0.7	2.634	3.76
0.8	3.070	3.84
0.9	3.540	3.93
1.0	4.100	4.10
2.0	9.937	4.97
3.0	18.100	6.03
4.0	30.5	7.62
5.0	44.0	8.80
6.0	61.0	10.16

Table LVI.—Conductivity Measurements.

$\mu_\infty\ 0^\circ = 240.5.$

v.	$\mu_v\ 0^\circ$.	α.
0.166	83.05	34.5
0.20	100.2	41.7
0.25	120.2	50.0
0.33	141.1	58.7
0.50	166.6	69.3
1.00	191.0	79.4
1.11	196.0	81.5
1.25	200.5	83.4
1.43	204.0	84.8
1.66	208.0	86.5
2.00	209.5	87.1
2.50	214.0	89.0
3.33	217.0	90.2
5.00	218.0	90.6
10.00	228.5	95.0
20.00	234.0	97.3

Table LVII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0017	0.0456	24.9551	0.18
0.1	25.0250	0.0911	24.9339	0.26
0.2	25.0716	0.1823	24.8893	0.44
0.3	25.1148	0.2734	24.8414	0.63
0.4	25.1289	0.3646	24.7643	0.94
0.5	25.1712	0.4557	24.7155	1.14
0.6	25.1949	0.5469	24.6480	1.41
0.7	25.2428	0.6380	24.6048	1.58
0.8	25.3075	0.7292	24.5783	1.69
0.9	25.3659	0.8203	24.5456	1.82
1.0	25.4510	0.9115	24.5395	1.84
2.0	25.7906	1.8230	23.9676	4.13
3.0	26.1606	2.7345	23.4261	6.30
4.0	26.5373	3.6460	22.8913	8.43
5.0	26.8555	4.5575	22.2980	10.81
6.0	27.2191	5.4690	21.7501	13.00

Table LVIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.972	3.67	3.59	3.58	—	—
0.1	0.950	3.63	3.55	3.54	—	—
0.2	0.906	3.55	3.56	3.54	—	—
0.3	0.902	3.54	3.60	3.58	0.62	2.07
0.4	0.890	3.51	3.60	3.57	0.89	2.24
0.5	0.871	3.48	3.66	3.62	2.13	4.26
0.6	0.865	3.47	3.75	3.70	3.44	5.74
0.7	0.848	3.44	3.76	3.70	3.90	5.58
0.8	0.834	3.41	3.84	3.78	5.44	6.80
0.9	0.815	3.37	3.93	3.86	7.05	7.83
1.0	0.794	3.34	4.10	4.02	9.40	9.40
2.0	0.693	3.15	4.98	4.77	18.86	9.43
3.0	0.586	2.95	6.03	5.65	26.55	8.85
4.0	0.500	2.79	7.62	6.98	33.35	8.34
5.0	0.417	2.64	8.80	7.85	36.87	7.37
6.0	0.345	2.49	10.16	8.84	39.91	6.65

Hydrobromic Acid.

The hydrobromic acid was kindly prepared for us by Professor Renouf. A fairly wide range of concentration was investigated. The results were very similar in character to those obtained with hydrochloric acid. The solutions up to about 0.3 N show no hydration. The hydration from this point to the most concentrated solution investigated, is of the same order as for hydrochloric acid (see Fig. III.).

The number of molecules of water in combination with 1 molecule of the acid is of the same magnitude with hydrobromic as with hydrochloric acid. It increases from about 0.3 N to 2 N and then decreases up to the most concentrated solution used. The meaning of this rather surprising fact will be pointed out in the general discussion of the results.

Table LIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1229	0°.451	3.67
0.1843	0°.657	3.56
0.2467	0°.880	3.57
0.3686	1°.350	3.69
0.4914	1°.845	3.75
0.614	2°.316	3.77
1.229	5°.440	4.42
1.843	9°.200	4.99
2.457	15°.0	6.10
3.072	21°.5	7.00
3.686	29°.0	7.87
4.30	41°.0	9.54

Table LX.—Conductivity Measurements.

$\mu\infty\ 0° = 246.$

v.	μ_v 0°.	α.
0.23	115.8	47.1
0.27	129.3	52.6
0.33	145.8	59.3
0.41	171.0	69.5
0.54	174.7	71.0
0.82	194.2	78.9
1.63	211.7	86.1
2.03	220.3	89.6
2.71	224.0	91.1
4.07	227.5	92.5
5.43	230.5	93.7
8.14	238.2	96.8
16.28	244.0	99.2

Table LXI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.0614	25.0575	0.1243	24.9332	0.27
0.1229	25.1350	0.2487	24.8863	0.46
0.1843	25.2025	0.3730	24.8295	0.68
0.2457	25.2800	0.4973	24.7827	0.87
0.3686	25.4050	0.7460	24.6590	1.36
0.4914	25.5450	0.9946	24.5504	1.80
0.6143	25.7025	1.2433	24.4592	2.16
1.229	26.3925	2.4875	23.9050	4.38
1.843	27.0825	3.7302	23.3523	6.59
2.457	27.7850	4.9730	22.8120	8.75
3.072	28.4500	6.2177	22.2323	11.07
3.686	29.1525	7.4605	21.6920	13.23
4.300	29.8275	8.7032	21.1243	15.50
5.7297	31.4600	11.5075	19.9525	20.19

Table LXII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L'.	*m'*.	H.
0.0614	0.992	3.71	..	..	—	—
0.1229	0.968	3.66	3.67	3.65	—	—
0.1843	0.937	3.60	3.56	3.54	—	—
0.2457	0.925	3.58	3.57	3.54	—	—
0.3686	0.911	3.55	3.69	3.64	1.67	4.53
0.4914	0.896	3.53	3.75	3.68	2.22	4.52
0.6143	0.861	3.46	3.77	3.69	3.50	5.70
1.229	0.789	3.33	4.42	4.23	11.82	9.62
1.843	0.710	3.18	4.99	4.66	17.65	9.58
2.457	0.695	3.15	6.10	5.57	24.10	9.80
3.072	0.593	2.96	7.00	6.23	29.17	9.48
3.686	0.526	2.84	7.87	6.83	32.40	8.79
4.300	0.471	2.74	9.54	8.06	36.65	8.52

Nitric Acid.

The results with nitric acid are of the same general character as those with hydrochloric and hydrobromic acids. The freezing-point lowerings are, however, less in the case of nitric acid and, since the dissociation is about the same, the hydrating power is smaller.

Like hydrochloric and hydrobromic acids, dilute solutions of nitric acid seem to form no hydrates. Not until about 0.7 N is reached, is there manifested any appreciable power to combine with water. The total amount of water combined with the acid increases with the concentration up to the most concentrated solution.

The number of molecules of water in combination with 1 molecule of the acid increases from about 0.7 N, with the concentration, to about 4 N and then begins to decrease with further increase in the concentration.

Table LXIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.175	3.51
0.10	0°.350	3.50
0.20	0°.696	3.48
0.30	1°.05	3.50
0.40	1°.415	3.54
0.50	1°.79	3.58
0.60	2°.20	3.66
0.70	2°.59	3.70
0.80	3°.00	3.75
0.90	3°.39	3.77
1.00	3°.806	3.806
2.00	8°.410	4.205
3.00	13°.908	4.636
4.00	23°.00	5.75
5.00	32°.50	6.50
6.00	42°.00	7.00

Table LXIV.—Conductivity Measurements.

μ_∞ 0° = 235.6.

v.	μ_v 0°.	α.
0.166	89.4	37.9
0.20	108.0	45.8
0.25	127.1	53.9
0.33	148.9	63.2
0.50	174.0	73.9
1.00	199.5	84.8
1.11	204.0	86.7
1.25	205.5	87.3
1.43	207.0	88.0
1.66	209.2	88.9
2.00	215.0	91.2
2.50	218.6	92.8
3.33	222.1	94.3
5.00	226.1	96.0
10.00	228.5	97.0
20.00	232.5	98.7

Table LXV.—Specific Gravity Measurements.

m.	$W_{\text{Sol.}}$	$W_{\text{Acid.}}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0150	0.0788	24.9362	0.26
0.1	25.0575	0.1576	24.8999	0.40
0.2	25.1425	0.3153	24.8272	0.69
0.3	25.2250	0.4729	24.7521	0.99
0.4	25.3050	0.6305	24.6745	1.30
0.5	25.3900	0.7881	24.6019	1.55
0.6	25.4750	0.9458	24.5292	1.88
0.7	25.5825	1.1034	24.4791	2.08
0.8	25.6400	1.2610	24.3790	2.48
0.9	25.6953	1.4186	24.2767	2.89
1.0	25.7700	1.5763	24.1937	3.23
2.0	25.6193	3.1525	23.4668	6.13
3.0	27.4660	4.7287	22.7373	9.05
4.0	28.2364	6.3050	21.9314	12.25
5.0	29.0029	7.8813	21.1216	15.51
6.0	29.7758	9.4575	20.3183	18.73

Table LXVI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.987	3.70	3.51	3.50	—	—
0.1	0.970	3.66	3.50	3.49	—	—
0.2	0.960	3.65	3.48	3.46	—	—
0.3	0.943	3.61	3.50	3.47	—	—
0.4	0.928	3.59	3.54	3.49	—	—
0.5	0.912	3.56	3.58	3.52	—	—
0.6	0.889	3.51	3.66	3.59	1.24	2.07
0.7	0.880	3.50	3.70	3.62	1.84	2.63
0.8	0.873	3.48	3.75	3.66	2.73	3.41
0.9	0.867	3.47	3.77	3.66	2.88	3.20
1.0	0.848	3.44	3.81	3.69	3.76	3.76
2.0	0.739	3.23	4.21	3.95	10.13	5.06
3.0	0.632	3.04	4.64	4.22	15.53	5.18
4.0	0.539	2.86	5.75	5.05	24.09	6.02
5.0	0.458	2.61	6.50	5.49	29.14	5.83
6.0	0.379	2.56	7.00	5.69	30.56	5.09

Phosphoric Acid.

The freezing-point lowerings produced by phosphoric acid are so small that, although the dissociation is not large, the amount of hydration is small, manifesting itself only in the more concentrated solutions.

Table LXVII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.1	0°.235	2.35
0.2	0°.458	2.29
0.3	0°.667	2.22
0.4	0°.868	2.17
0.6	1°.292	2.15
0.8	1°.775	2.22
1.0	2°.370	2.37
2.0	5°.550	2.77
3.0	9°.75	3.25
4.0	16°.50	4.12
5.0	25°.00	5.00
6.0	38°.00	6.33
6.919	52°.00	7.52

Table LXVIII.—Conductivity Measurements.

μ_∞ 0° = 240.

v.	μ_v 0°.	α.
0.14	20.00	8.3
0.16	23.4	9.8
0.20	26.8	11.2
0.25	31.6	14.3
0.33	35.2	14.7
0.50	38.0	16.1
1.00	42.0	17.5
1.11	42.6	17.8
1.25	43.0	17.9
1.43	44.4	18.3
1.66	45.1	18.8
2.00	45.8	19.1
2.50	47.5	19.8
3.33	50.0	20.8
5.00	61.5	25.6
10.00	68.6	28.6
20.00	85.5	35.6

Table LXIX.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0550	0.1225	24.9325	0.27
0.10	25.1025	0.2450	24.8575	0.57
0.20	25.2425	0.4900	24.7525	0.99
0.30	25.3750	0.7350	24.6400	1.44
0.40	25.5075	0.9800	24.5275	1.89
0.50	25.6375	1.2250	24.4125	2.35
0.60	25.7650	1.4700	24.2950	2.82
0.6916	25.9100	1.6952	24.2148	3.14
0.80	26.0200	1.9600	24.0600	3.76
0.90	26.1575	2.2050	23.9525	4.29
1.00	26.2900	2.4500	23.8400	4.64
2.00	27.6175	4.9000	22.7175	9.13
3.00	28.8875	7.3500	21.5375	13.85
4.00	31.1775	9.8000	21.2775	18.89
5.00	31.4975	12.2500	19.2475	23.01
6.00	32.7050	14.7000	18.0050	27.98
6.919	33.5725	16.9516	16.6209	33.52

Table LXX.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.1	0.286	3.46	2.35	2.34	—	—
0.2	0.256	3.29	2.29	2.27	—	—
0.3	0.208	3.02	2.22	2.19	—	—
0.4	0.198	2.96	2.17	2.13	—	—
0.6	0.188	2.91	2.15	2.09	—	—
0.8	0.179	2.86	2.22	2.14	—	—
1.0	0.175	2.84	2.37	2.26	—	—
2.0	0.161	2.76	2.77	2.52	—	—
3.0	0.147	2.68	3.25	2.80	2.38	0.79
4.0	0.143	2.66	4.12	3.33	11.18	2.79
5.0	0.112	2.48	5.00	3.85	19.77	3.95
6.0	0.098	2.41	6.33	4.56	26.19	4.37
6.919	0.083	2.32	7.52	5.00	29.78	4.34

Chromic Acid.

Chromic acid gives large freezing-point lowerings at all of the dilutions studied and, not being very highly dissociated, it therefore has great power to form hydrates. As Ostwald pointed out, chromic acid exists in solution, in the form of dichromic acid, the hydrogen ions effecting the transformation. The amount of combined water increases regularly with the concentration (see Fig. IV.) and the amount of water in combination with 1 molecule of the acid increases, in general, with the dilution of the solution.

Table LXXI.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.10	$0^{\circ}.526$	5.26
0.15	$0^{\circ}.775$	5.16
0.20	$1^{\circ}.050$	5.24
0.30	$1^{\circ}.610$	5.36
0.40	$2^{\circ}.22$	5.54
0.50	$2^{\circ}.89$	5.78
1.00	$6^{\circ}.78$	6.78
1.50	$11^{\circ}.47$	7.64
2.00	$16^{\circ}.00$	8.00
2.50	$22^{\circ}.5$	9.00
3.00	$31^{\circ}.0$	10.40
3.50	$42^{\circ}.0$	12.00
4.00	$57^{\circ}.5$	14.40

Table LXXII.—Conductivity Measurements.

$\mu\infty\ 0° = 523$.

v.	μ_v 0°.	α.
0.286	108.4	20.7
0.333	128.2	24.5
0.400	157.3	30.0
0.500	206.8	39.3
0.666	256.2	49.0
1.000	312.4	59.7
2.000	374.3	71.6
2.500	388.9	74.3
3.33	410.0	78.4
5.00	420.0	80.3
6.66	428.0	81.8
10.00	436.0	83.4
20.00	440.0	84.1
40.00	452.0	86.4

Table LXXIII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Acid.}$	$W_{H_2O.}$	Correction. Per cent.
0.10	25.3425	0.5456	24.7969	0.81
0.15	25.5125	0.8184	24.6941	1.22
0.20	25.6900	1.0912	24.5988	1.60
0.30	26.0375	1.6368	24.4007	2.00
0.40	26.3875	2.1824	24.2051	3.18
0.50	26.7300	2.7277	24.0023	3.99
1.00	28.4350	5.4555	22.9795	8.08
1.50	30.0950	8.1833	21.9117	12.35
2.00	31.7625	10.9110	20.8515	16.59
2.50	33.3800	13.6388	19.7412	21.03
3.00	34.9825	16.3665	18.6160	25.54
3.50	36.6100	19.0943	17.5157	29.94
4.00	38.2475	21.8220	16.4255	34.30

Table LXXIV.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	*m*′.	H.
0.10	0.834	4.96	5.26	5.22	2.78	27.8
0.15	0.818	4.90	5.16	5.10	2.18	14.5
0.20	0.803	4.85	5.24	5.16	3.33	16.7
0.30	0.784	4.78	5.36	5.25	4.92	16.4
0.40	0.743	4.62	5.54	5.36	7.67	19.2
0.50	0.716	4.52	5.78	5.55	10.31	20.6
1.00	0.597	4.08	6.78	6.23	19.17	19.17
1.50	0.490	3.68	7.64	6.70	25.05	16.7
2.00	0.393	3.32	8.00	6.67	27.90	13.95
2.50	0.300	2.98	9.00	7.11	32.38	12.95
3.00	0.245	2.87	10.40	7.74	34.95	11.65
3.50	0.207	2.63	12.00	8.41	38.18	10.9
4.00	0.134	2.36	14.40	9.46	41.75	10.4

Sodium Hydroxide.

Sodium hydroxide was studied over as wide range of concentration as the solubility would permit. From solutions more concentrated than 6 N the solid separated. The material used was free from carbonate and the solutions were kept in closed vessels during all of the work.

The amount of water combined passes through a minimum (see Fig. V.) at a concentration of about 0.3 N. From this point it increases with the concentration up to the most concentrated solution. The number of molecules of water in

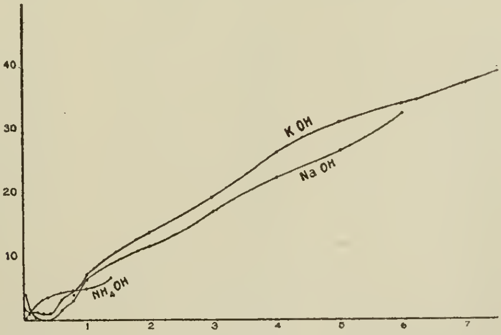

Fig. V.

combination with one of the dissolved substance also passes through a minimum.

Table LXXV.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.188	3.76
0.1	0°.358	3.58
0.2	0°.693	3.47
0.3	0°.992	3.31
0.4	1°.334	3.34
0.6	2°.030	3.38
0.8	2°.727	3.41
1.0	3°.465	3.465
2.0	7°.40	3.70
3.0	11°.75	3.92
4.0	17°.00	4.25
5.0	23°.00	4.60
6.0	33°.00	5.50

Table LXXVI.—Conductivity Measurements.

$\mu\infty$ 0° = 138.6.

v.	μ_v 0°.	α.
0.125	16.07	11.6
0.143	21.67	15.6
0.166	29.28	21.1
0.200	38.27	27.6
0.250	49.67	35.8
0.333	62.3	44.9
0.500	78.5	57.0
1.00	95.5	63.7
1.25	101.0	71.9
1.66	105.0	75.0
2.50	110.0	79.1
3.33	113.0	81.3
5.00	117.0	83.2
10.00	119.0	85.5
20.00	121.0	87.0

Table LXXVII.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Base.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0550	0.0501	25.0049	—0.02
0.10	25.1000	0.1002	24.9998	0.00
0.20	25.2125	0.2003	25.0122	—0.05
0.30	25.3125	0.3005	25.0120	—0.05
0.40	25.4125	0.4006	25.0119	—0.05
0.60	25.6175	0.6009	25.0166	—0.07
0.80	25.8200	0.8012	25.0188	—0.07
1.00	26.0175	1.0015	25.0160	—0.06
2.00	26.9875	2.0030	24.9845	0.06
3.00	27.8925	3.0045	24.8880	0.45
4.00	28.8300	4.0060	24.8240	0.70
5.00	29.5650	5.0075	24.5575	1.77
6.00	30.3225	6.0090	24.3135	2.35
7.00	31.0900	7.0105	24.0795	3.68
8.00	31.8025	8.0120	23.7905	4.84

Table LXXVIII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.870	3.48	3.76	3.76	4.16	83.2
0.10	0.855	3.45	3.58	3.58	2.06	20.6
0.20	0.832	3.42	3.47	3.47	0.87	4.3
0.30	0.813	3.37	3.31	3.31	—	—
0.40	0.791	3.33	3.33	3.33	—	—
0.60	0.750	3.25	3.38	3.38	2.11	3.5
0.80	0.719	3.20	3.41	3.41	3.44	4.3
1.0	0.637	3.04	3.465	3.465	6.83	6.8
2.0	0.570	2.92	3.70	3.70	11.72	5.86
3.0	0.449	2.70	3.92	3.90	17.05	5.68
4.0	0.358	2.53	4.25	4.23	22.33	5.58
5.0	0.276	2.37	4.60	4.52	26.44	5.28
6.0	0.211	2.25	5.50	5.37	32.26	5.37

Potassium Hydroxide.

Potassium hydroxide, free from carbonate, was carefully preserved during the investigation in closed vessels. It could be used up to a concentration that was about 8 N.

The total amount of combined water passes through a minimum at a concentration of about 0.3 N. Similarly, the number of molecules of water in combination with 1 molecule of the base. In general behavior, respecting its power to combine with water, potassium hydroxide is, then, strictly analogous to sodium hydroxide.

Table LXXIX.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0°.183	3.66
0.1	0°.357	3.57
0.2	0°.710	3.55
0.3	1°.050	3.50
0.4	1°.390	3.475
0.6	2°.143	3.571
0.8	2°.885	3.606
1.0	3°.773	3.773
2.0	8°.42	4.21
3.0	14°.0	4.66
4.0	22°.5	5.62
5.0	32°.5	6.50
6.0	43°.5	7.25
7.0	57°.5	8.21
8.0	76°.0	9.50

Table LXXX.—Conductivity Measurements.

μ_∞ 0° = 154.29.

v.	μ_v 0°.	α.
0.111	32.25	20.9
0.125	38.77	25.1
0.143	48.65	31.5
0.166	56.19	36.4
0.200	65.74	42.6
0.250	77.60	50.6
0.333	88.85	58.2
0.500	102.31	66.3
1.000	116.94	75.9
1.250	118.0	76.5
1.660	123.0	79.7
2.500	126.0	82.3
3.333	128.0	83.6
5.000	131.0	85.5
10.00	132.5	86.5
20.00	136.0	89.0

Table LXXXI.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Base.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	25.0750	0.0702	25.0048	—0.02
0.10	25.1250	0.1404	24.9846	0.06
0.20	25.2500	0.2808	24.9692	0.12
0.30	25.3750	0.4212	24.9538	0.18
0.40	25.4925	0.5616	24.9309	0.28
0.60	25.7373	0.8424	24.8949	0.42
0.80	25.9700	1.1232	24.8458	0.62
1.0	26.2050	1.4040	24.8010	0.80
2.0	27.3150	2.8080	24.5070	1.97
3.0	28.3500	4.2120	24.1380	3.45
4.0	29.4025	5.6160	23.7865	4.85
5.0	30.3600	7.0200	23.3400	6.64
6.0	31.2675	8.4240	22.8435	8.63
7.0	32.1825	9.8280	22.3545	10.58
8.0	33.3075	11.2320	22.0755	11.71

Table LXXXII.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	*m*′.	H.
0.05	0.890	3.52	3.66	3.66	2.11	42.2
0.10	0.865	3.47	3.57	3.57	1.56	15.6
0.20	0.855	3.45	3.55	3.55	1.56	7.8
0.30	0.836	3.41	3.50	3.49	1.28	4.3
0.40	0.823	3.39	3.475	3.47	1.28	3.2
0.60	0.797	3.34	3.57	3.56	3.42	5.7
0.80	0.765	3.28	3.61	3.58	4.67	5.8
1.0	0.759	3.27	3.77	3.74	6.94	6.9
2.0	0.663	3.09	4.21	4.13	14.05	7.0
3.0	0.582	2.94	4.66	4.50	19.28	6.4
4.0	0.506	2.80	5.63	5.36	26.55	6.6
5.0	0.426	2.65	6.50	6.07	31.15	6.2
6.0	0.364	2.54	7.25	6.63	34.30	5.7
7.0	0.315	2.45	8.21	7.34	37.00	5.3
8.0	0.251	2.33	9.50	8.39	40.10	5.0

Ammonium Hydroxide.

Ammonium hydroxide was studied in a manner similar to the other bases. The freezing-point lowerings were small but, since the dissociation is so very slight, it, nevertheless, demonstrates the possession, by this compound, of some power to combine with water.

The amount of combined water increases from the most dilute to the most concentrated solutions (see Fig. V.). The amounts of water combined with 1 molecule of the base, while somewhat irregular, in general, increases with the dilution.

Table LXXXIII.—Freezing-point Measurements.

m.	Δ.	$\frac{\Delta}{m}$.
0.05	0.0961	1.92
0.10	0.192	1.92
0.20	0.384	1.92
0.30	0.591	1.97
0.40	0.791	1.98
0.60	1.191	1.98
0.80	1.585	1.98
1.00	1.995	1.995
1.4036	2.865	2.04

Table LXXXIV.—Conductivity Measurements.

$\mu\infty\ 0^\circ = 154\ 69.$

v.	$\mu_v\ 0^\circ$.	α.
1.0	0.41	0.26
1.25	0.59	0.38
1.66	0.76	0.49
2.50	0.93	0.60
$3.3\dot{3}$	1.08	0.70
5.00	1.34	0.86
10.00	1.84	1.19
20.00	2.56	1.66

Table LXXXV.—Specific Gravity Measurements.

m.	$W_{Sol.}$	$W_{Base.}$	$W_{H_2O.}$	Correction. Per cent.
0.05	24.9775	0.0426	24.9349	—0.26
0.10	24.9625	0.0852	24.8773	—0.49
0.20	24.9425	0.1704	24.7721	—0.91
0.30	24.9250	0.2556	24.6694	—1.32
0.40	24.9050	0.3408	24.5642	—1.74
0.60	24.8625	0.5112	24.3513	—2.59
0.80	24.8250	0.6816	24.1434	—3.43
1.00	24.7925	0.8520	23.9405	—4.21
1.4036	24.7150	1.1928	23.5222	—5.91

Table LXXXVI.—Hydrates.

m.	α.	L.	$\frac{\Delta}{m}$.	L′.	m'.	H.
0.05	0.0166	1.89	1.92	1.92	0.87	17.4
0.10	0.0119	1.88	1.92	1.93	1.73	17.3
0.20	0.0086	1.88	1.92	1.94	1.72	8.6
0.30	0.0070	1.87	1.97	2.00	3.61	12.0
0.40	0.0060	1.87	1.98	2.01	3.82	9.5
0.60	0.0049	1.87	1.98	2.03	4.38	7.3
0.80	0.0038	1.87	1.98	2.05	4.88	6.1
1.00	0.0026	1.86	1.995	2.08	5.88	5.9
1.4036	—	1.86	2.04	2.16	7.72	5.5

General Discussion of Results.

The amount of work that has now been done in this field, *involving between 90 and 100 compounds and between 1,200 and 1,500 solutions*, seems to make it desirable, if not absolutely necessary, to take a general survey of the subject at the present stage of the investigation. This is all the more needful, in that the various papers have been published in different scientific journals.

The whole work was the outcome of observations made in this laboratory, about 6 years ago, by Jones and Ota[1] and Jones and Knight;[2] that certain salts, in concentrated solution, give abnormally great lowering of the freezing-point of water. The problem was taken up by Jones and Chambers[3] and studied for a number of chlorides and bromides. As the result of this work Jones[4] concluded that "In concentrated solutions these chlorides and bromides must take up a part of the water forming complex compounds with it, and thus removing it from the field of action as far as freezing-point lowering is concerned. The compound, which is probably very unstable, formed by the union of a molecule of the chloride or bromide with a large number of molecules of water, acts as a unit or as one molecule in lowering the freezing-point of the remaining water. The total amount of water present, which is now acting as solvent, is diminished by the amount taken up by the chloride or bromide molecules. The lowering of the freezing-point is thus abnormally great, because a part of the water is no longer present as solvent, but is in combination with the chloride or bromide molecules. By assuming that a molecule of the halide is in combination with a large number of molecules of water, it is possible to explain all the freezing-point results obtained.'' At the suggestion of Jones, this work was continued by Chambers and Frazer,[1] and results of the same general character were obtained.

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[1] This Journal, **22**, 5 (1899).

[2] *Ibid.*, **22**, 110 (1899).

[3] *Ibid.*, **23**, 89 (1900).

[4] *Ibid.*, **23**, 103 (1900).

The investigation was then taken up in a more systematic manner by Jones and Getman.[2] They studied a variety of acids, bases and salts and found that the phenomenon previously observed was general—most substances giving, in concentrated solutions, freezing-point lowerings that were greater than the theoretical value.

In the following year, Jones and Getman, aided by a grant from the Carnegie Institution, continued their former work and calculated the approximate composition of the hydrates formed by a number of substances.[3]

Through another grant from the Carnegie Institution, Jones and Bassett have still further continued the work. They have had to do especially with the determination, as closely as possible, of the composition of the hydrates formed. The first part of this investigation has already been recorded;[4] the results of the second part are contained in this paper.

Evidence for the Existence of Hydrates in Solution.

Four distinct lines of evidence bearing upon the hydrate theory have been pointed out. In the first place, the *minima in the boiling-point curves manifest themselves at greater concentrations than in the freezing-point curves.* This is just what would be expected in terms of our hydrate theory, since, at the higher temperatures, the hydrates would be less stable and a greater concentration would have to be reached before there was sufficient hydration to change the direction of the curve and produce a minimum.

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[1] This Journal, **23**, 512 (1900).

[2] Z. physik. Chem., **46**, 244 (1903). This Journal, **27**, 433 (1902).

[3] This Journal, **31**, 303 (1904); **32**, 308 (1904). Z. physik. Chem., **49**, 385 (1904).

[4] This Journal, **33**, 534 (1905).

The second line of evidence, which is more direct, has to do with the *relation between water of crystallization and lowering of the freezing-point.* This has already been pointed out.[1] Curve plates have been drawn, which show this relation very clearly. The chlorides stand in the same order with respect to their power to lower the freezing-point of water and with respect to their power to combine with water, as water of crystallization. The same relation holds for the various bromides and iodides that have been investigated.

Turning to the nitrates, the relations are just as satisfactory. When all of the nitrates with which we have worked are plotted on the same curve sheet, the ordinates being molecular lowerings of the freezing-point and the abscissas concentrations, we find a most satisfactory relation between water of crystallization and molecular lowering of the freezing-point.

In the above comparisons the acid is kept constant in every case and the salts of it with the different metals are compared with one another. It has also been shown[2] that similar relations exist between the salts of any given metal with different acids. If we compare the chlorides, bromides, iodides and nitrates of any given metal, having the same number of molecules of water of crystallization, they give just about the same molecular lowering of the freezing-point of water. As such comparisons have so recently been discussed,[3] reference only will be made to them.

The relation just referred to is exactly what would be expected if our hydrate theory is true. Indeed, it is difficult to see in what other way it can be interpreted. The relation is closer and much more comprehensive than we could ever have anticipated. In the building up of crystals, the exact geometrical shape of the molecules is undoubtedly a fundamental matter and this would condition, to some extent, the number of molecules of water with which any given salt would crystallize. Notwithstanding this and other influences which affect the molecules as they build up crystals, relations, such as those already pointed out, manifest themselves very clearly.

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[1] This JOURNAL, **31**, 344 (1904). Z. physik. Chem., **49**, 385 (1904). THIS JOURNAL, **32**, 308 (1904); **33**, 534 (1905). J. Chim. Phys., **3**, 455 (1905).

[2] THIS JOURNAL, **33**, 540 (1905).

[3] *Ibid.*, **33**, 541 (1905).

Again, we have searched for a salt with a larger number of molecules of water of crystallization than that possessed by the nitrates of chromium and iron, which is 9, and which would be adapted to our work. The salts of chromic and dichromic acids would not help us, since these, like the sulphates, probably undergo polymerization in solution and would give abnormal results. The best example that we could find was disodium phosphate, with 12 molecules of water of crystallization. The unfortunate feature in connection with this salt is its slight solubility in water, especially at the freezing temperature. We were able to work at two concentrations, 0.05 and 0.1 N and, although the experimental error at these high dilutions is relatively large, we feel justified in drawing the conclusion that this salt has greater power to combine with water than any other compound which we have studied.

Two other lines of evidence bearing upon our hydrate theory, the one having to do with the effect of temperature upon water of crystallization and the other with certain changes in color produced in solution, have already been discussed in the earlier part of this paper and will, therefore, be only referred to here. The reaction between crystallized calcium chloride and an aqueous solution of cobalt chloride shows, conclusively, that a salt can combine with more water in solution than it can bring with it out of solution, as water of crystallization.

Composition of the Hydrates.

The work of the present year has had to do with the determination of the composition of the hydrates formed by the various substances at the different dilutions. While certain assumptions are necessary in making these calculations, yet, taking all things into account, it seems to us probable that we can calculate the approximate composition of the hydrates that exist in the aqueous solutions. The method of calculation has already been discussed. It, therefore, remains only to consider the results, the most reliable of which are contained in the paper recently published[1] and in the present communication.

If we examine these results, we shall see that the total amount of water held in combination by the dissolved substance increases with the concentration of the solution. This is, of course, what would be expected from the law of mass action. If we examine column "*m*'" in the "Hydrate" tables we shall see how general this relation is. There are comparatively few deviations from this relation, with the exception of some dilute solutions where the experimental errors are necessarily large.

If we turn to column "H" in the "Hydrate" tables, we have the number of molecules of water combined with 1 molecule of the dissolved substance. The general relation here is, that the number of molecules of water combined with 1 molecule of the dissolved substance, increases with the dilution, from the most concentrated to the most dilute solution investigated. This is shown by such substances as magnesium chloride, magnesium bromide, manganese chloride, nickel chloride, nickel nitrate, copper chloride, strontium nitrate, chromium chloride, sodium ammonium acid phosphate and others. In some cases irregularities manifest themselves, but these are, doubtless, often due to a summation of experimental errors.

If we turn to the acids a different relation appears. Take hydrochloric, hydrobromic, nitric and sulphuric acid.[2] Starting with the more concentrated and passing to the more dilute solutions, we find that the number of molecules of water in combination with 1 molecule of the acid, passes through a maximum. In the case of the four acids already mentioned, this maximum is reached at about 2 N solution.

A possible explanation of this phenomenon, which is in keeping with the law of mass action, is the following: If the attraction of the dissolved molecule for water is slight then, when a certain dilution is reached, the effect of the presence of more water might actually diminish the amount of water combined with a molecule of the dissolved substance. When the number of molecules of water had become sufficiently great, their attractions for one another would summate, and might overcome, in part, the attraction of the dissolved substance for the water. In this case the *complexity of the hydrate would pass through a maximum and then decrease with further dilution.*

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[1] THIS JOURNAL, **33**, 534 (1905).

[2] *Ibid.*, **33**, 581 (1905).

Most of the organic compounds studied by Jones and Getman[1] show little or no power to combine with water. Glycerol, however, is a marked exception and cane-sugar also has considerable hydrating power. The total amount of water combined with the dissolved substance, in both cases, increases with the concentration, as we should expect. The number of molecules of water combined with 1 molecule of the dissolved substance, in the case of glycerol, increases, with a fair degree of regularity, with the dilution of the solution.

A number of organic acids were studied and shown to have little or no power to combine with water.

Both molecules and ions combine with water. Our opinion on this point has changed from time to time as the work has developed. Since such non-electrolytes as glycerol and cane-sugar can form hydrates, it is obvious that molecules can combine with water, because there are no ions present in such solutions. In the case of electrolytes, on the other hand, we frequently have the greatest hydration in the most dilute solutions. In such solutions there are very few molecules present, nearly all of them being broken down into ions. It is evident that the ions can combine with water. Our final conclusion is that both molecules and ions can combine with water and form hydrates.

The present theory of hydrates differs fundamentally from the older theory. It may not be obvious, at first sight, how the hydrate theory proposed by Jones differs from the older hydrate theory of Mendeléeff. A moment's thought, however, will show that the two are fundamentally different. According to the view of Mendeléeff, a compound such as calcium chloride or sulphuric acid, with water, forms three or four hydrates, having perfectly definite compositions and containing very different amounts of water; *e. g.*, $H_2SO_4.H_2O$; $H_2SO_4.2H_2O$; $H_2SO_4.6H_2O$; $H_2SO_4.150H_2O$. These hydrates and no intermediate ones, exist.

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[1] This Journal, **32**, 308 (1904).

According to the present theory, a compound such as calcium chloride *can form all the possible hydrates with water, from one or a few molecules of water up to at least 30 molecules.* The composition of the hydrate is conditioned by the concentration of the solution, temperature being constant.

It is possible, indeed, quite probable, that several hydrates, having different compositions, exist simultaneously in every solution. We cannot, of course, distinguish between this possibility and the simpler one—that at any given concentration only one hydrate, with a perfectly definite composition, exists.

Work by the boiling-point method has shown that dissolved substances can combine with solvents other than water. This has been demonstrated by Jones and Getman[1] to be the case with at least methyl and ethyl alcohols.

Summary of the Conclusions Thus Far Reached.

1. This investigation has already been extended to between 90 and 100 compounds, including salts, acids and bases, and between 1,200 and 1,500 solutions have been studied.

2. The freezing-point, the conductivities at 0° and the specific gravities of all the solutions have been measured, and the refractivity of a large number of them.

3. Four lines of evidence bearing upon the hydrate theory have been deduced and all of these point to its general correctness. These are, the relative positions of the minima in the freezing-point and in the boiling-point curves; the relation between water of crystallization and lowering of the freezing-point; the effect of temperature of crystallization on the amount of water of crystallization, and the power of substances to combine with more water in solution than they can bring with them out of solution, as shown by the change in color of

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[1] THIS JOURNAL, **31**, 339 (1904); **32**, 338 (1904).

a solution of cobalt chloride when shaken with crystallized calcium chloride.

4. The approximate composition of the hydrates formed by a fairly large number of electrolytes and some non-electrolytes have been calculated. Those substances that crystallize without water have little or no hydrating power. In general, the larger the number of molecules of water of crystallization the greater the hydrating power of the salt.

5. The total amount of water in combination with the dissolved substance increases with the concentration of the solution. The number of molecules of water in combination with 1 molecule of the dissolved substance usually increases with the dilution of the solution.

6. In some cases, as with the more common acids, the amount of water in combination with 1 molecule of the dissolved substances passes through a maximum as the dilution is increased. A possible explanation of this fact has been suggested.

7. A number of organic compounds have been studied, but only a few of these have been found to have any marked hydrating power.

8. Certain substances have been shown to have the power to combine with solvents other than water. Work, thus far, has been limited to methyl and ethyl alcohols.

9. It has been pointed out that the hydrates formed in aqueous solutions are unstable, especially at higher temperatures. They are, in general, broken down at the boiling-points of the solutions, all of the water escaping except what is held in combination by the salt, as water of crystallization.

10. As the result of our work as a whole, we must conclude that both molecules and ions have the power to combine with water in aqueous solutions and form hydrates.

11. The new hydrate theory differs fundamentally from the old, in that, according to the former, we have a series of hydrates formed by the dissolved substance having all possible compositions up to a given maximum—the composition depending on the concentration, as we should expect from the law of mass action.

12. The bearing of this work on the general theory of solutions is obvious. The fact that a part of the water is combined with the dissolved substance and is not acting as solvent water, must be taken into account in dealing with all solutions and especially with concentrated ones. This accounts, in large part, for the abnormal behavior of concentrated solutions and is, doubtless, an important factor in the apparent failure of the gas laws to apply to such solutions. When this is taken into account, together with such other factors as appear in Van der Waals' equation for gases, it will probably be shown that the gas laws apply to the osmotic pressures of concentrated solutions measured under comparable conditions with gases, as well as to concentrated gases.

This line of work is still in progress in this laboratory and will be continued for some time to come.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1905.

OBITUARY.

PER THEODOR CLEVE.

Professor Cleve was born at Stockholm, February 10, 1840, and died at Upsala, June 18, 1905. He graduated from the University of Upsala in 1863 and has held the chair of chemistry there since 1874. After graduation he studied under Wurtz and, before returning to Upsala, taught for 4 years in the Stockholm Polytechnic. Cleve's chemical activities covered a wide range, although he is best known for his work on the rare earth metals. We owe the discovery of thulium to him (1880), of scandium (1890) independently of Nilson and of helium (1895) independently of Ramsay. He was the first to observe the isomerism of the platinumamine derivatives. Cleve's scientific efforts were not confined to chemistry but included geology, botany and hydrography ; his contributions to general literature were also noteworthy. He received the Davy medal from the Royal Society in 1904, and was president of the committee for chemistry of the Nobel Trust.

REVIEWS.

ELEMENTS OF APPLIED MICROSCOPY. By CHARLES EDWARD AMORY WINSLOW, Instructor in Industrial Microscopy and Sanitary Biology in the Massachusetts Institute of Technology. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1905. pp. xii + 183. Price, $1.50.

This little work is intended especially for the use of beginners in microscopical examinations, but it will be also valuable to many experts. The first section describes the various parts of microscopic apparatus, care of eyes, etc., and will be especially useful for beginners, but Chapter III. and the following ones contain much that is helpful to workers in general. There is a large part of the book which is especially useful to those engaged in the examination of foods and fibers and, therefore, it is particularly valuable to workers in agricultural research. There are interesting chapters also on the microscope as applied to medicine, sanitation and to cases in courts, while the chapter on microchemistry will be of service to chemists in general. The chapter on petrography will be especially useful to those who are working with minerals and the chemistry or physics of materials used in road-making. The book contains 60 illustrations, which are of distinct advantage in the elucidation of the text. As is necessarily the case in a volume of this kind, the material is more for the purpose of illustration and suggestion than for detailed description or discussion.

The bibliography at the end of each chapter will refer the inquiring student to more exhaustive works and this feature of the book might have been made more extensive without adding materially to its size, while increasing its usefulness for advanced students. The character of those who are beginning the study of the microscope is so varied, representing as it does all stages from childhood to old age, that the preparation of a book of this character is an exceedingly difficult matter. The volume shows, however, that the author has covered this point and rendered his work helpful to students of almost every class. H. W. W.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEFF. Third English Edition translated from the Russian Seventh Edition by GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg, and edited by THOMAS H. POPE, B.SC., F.I.C., in two volumes. London and New York: Longmans, Green & Co. 1905. Price, $10.00 net.

The first edition of this work was reviewed 13 years ago by President Remsen.[1] While one finds new and interesting matter in this last edition, the character of the work remains unchanged. The foot-notes still form nearly half of the contents and are full of philosophical thought, of originality and suggestions.

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[1] THIS JOURNAL, 14, 251.

A quotation from the preface to this edition will show Mendeléeff's attitude :

"After having been an insignificant but zealous worker in chemistry for almost half a century, I wished that my book should retain some traces of how a confirmed disciple of Gerhardt regards the fundamental problems of the theory of the chemical elements at the beginning of the twentieth century. As an example, I may mention that the more I have thought on the nature of the chemical elements, the more decidedly have I turned away from the classical notion of a primary matter and from the hope of attaining the desired end by a study of electrical and optical phenomena and the more clearly have I recognized that first and foremost are needed truer conceptions of 'mass' and 'ether' than those in vogue at the present time. The return to electro-chemism, which is so evident in the supporters of the hypothesis of 'electrolytic dissociation,' and the notion of the splitting up of atoms into 'electrons,' in my opinion only complicate and in no way explain so real a matter as the chemical changes of substances, which led to the recognition of the invariable and ponderable atoms of simple bodies."

As Mendeléeff does not consider the hypothesis of electrolytic dissociation and the hypotheses deduced from it to be "in accordance with fact," and as he devotes much space in text and notes to osmotic pressure, nature of solutions, relation of gas and solution laws, it is very interesting to read his interpretation of facts from a point of view differing radically from that of Arrhenius and Ostwald.

One looks for his views on the subject of radioactive substances. In discussing them in a note under "Uranium" he says : "The greatest known concentration of mass of ponderable matter in the indivisible mass of the atom of uranium should already—*a priori*—produce peculiar qualities, although I am not in any way inclined (owing to the stern but fruitful discipline of inductive knowledge) to admit even the hypothetical transmutation of the elements into each other and see no possibility of argon or radio-active substances having originated from uranium, or conversely." It must be noted that this was published in Russia in 1902, prior to Ramsay's work on radium emanation and helium.

Enough has been said to point out the independent position which Mendeléeff holds, and it is this which makes his book so valuable and so fascinating to those who turn with weariness from the last repetition of what we all knew before of the average text-book. It is fair to say that most of these choice morsels are in the notes and Mendeléeff warns students against reading the notes, evidently thinking them too strong meat for chemical babes.

Appended to the translation are his Royal Institution lecture of 1889, his Faraday lecture of the same year on the periodic law and his recent essay on " An Attempt toward a Chemical Conception of the Ether." This last was quite recently reviewed by President Remsen.[1]

A few words may be given to the first of these lectures. Its object was to show that—" starting with Newton's third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities." He says, further on, " It will be seen that by the principle of substitution, that is, by the third law of Newton, we are able to deduce in the simplest manner not only the individual composition, the isomerism and relation of substances, but also the general laws which govern their most complex combinations without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double, or treble bonds which are so indispensable to structuralists in the explanation of the composition and construction of hydrocarbon compounds."

This, too, is very interesting coming from a pupil of Gerhardt, who never accepted the structural theories of Kekulé.

E. R.

MARCELI NENCKI OPERA OMNIA. Gesammelte Arbeiten von PROF. M. NENCKI. Braunschweig: Friedrich Vieweg und Sohn. 1905. Volume I., pp. 840; Volume II., pp. 893. Price, M. 45.

It is certainly a well-deserved honor to the memory of Nencki that this posthumous publication of his collected reprints should have appeared. The fact that it is edited by his ardent admirers and associates, Sieber and Zaleski, gives sufficient assurance of its accuracy and completeness. They have brought together the 346 widely scattered articles from Nencki's laboratory which appeared in German, French, Russian and Polish journals from 1869 to 1901. Of these articles Nencki's name is attached to somewhat less than half the number. The remainder appeared under the names of the many brilliant pupils attracted to the laboratory of this indefatigable worker, who prided himself on the fact that he was too busy to attend scientific meetings. As the subjects of the papers, however, were always suggested by Nencki and were executed under his supervision, it is only proper that they should appear in his "Opera Omnia." Although Nencki concerned himself with many different branches of science, organic chemistry, physiological chemistry, pharmacology, bacteriology and hygiene, his fame rests principally on his brilliant contributions to physiological chemistry. It is, indeed, difficult to give a just idea of Nencki's work within the limits of a review. His principal contributions to organic chemistry consisted in the synthesis of many compounds which he believed might throw light on physiological processes. Thus he synthesized many urea and guanidine derivatives, in connection with his work on the precursors of urea and its mode of formation in the body. The work of Nencki and his pupils on the decomposition-products of haemoglobin is classic. They showed haematoporphyrin to be isomeric with bilirubin, thus establishing, clearly, the derivation of the bile pigments from haemoglobin. They proved, further, that haemoglobin is closely related to chlorophyll and determined the structure of haomatoporphyrin and phylloporphyrin, from both of which they obtained haemopyrrol. This genetic and chemical relation so firmly established is, to be sure, of broad biological interest. Nencki's work on the chemical transformations of numerous aromatic substances in passing through the body, his work on the enzymes, putrefaction and immunity can only be mentioned here to give an idea of the scope of his work. While not a genius, Nencki represents the type of the brilliant investigator. The real advance in a science depends on the steady stream of such laborious researches as those executed in his aboratory.

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[1] THIS JOURNAL, **33**, 517.

An excellent photogravure of Nencki and a specimen page of his manuscript make the memorial a most complete, pleasing and impressive one. The work would be a valuable addition to any chemical or medical library.
A. S. L.

AVOGADRO AND DALTON. THE STANDING IN CHEMISTRY OF THEIR HYPOTHESES. By ANDREW M. MELDRUM, D.Sc. With a preface by FRANCIS R. JAPP, M.A., LL.D., F.R.S., Professor of Chemistry in the University of Aberdeen. Edinburgh: William F. Clay, 18 Teviot Place. 1904. Price, 3 Shillings, net.

In the preface Professor Japp says: "The important question whether, in discussing the constitution of matter, the atom or the molecule should be first considered is one regarding which there has been considerable difference of opinion among chemists." . . . . "In the study of the constitution of matter . . . . . we are compelled by the very nature of the particular problems of scientific measurement and calculation involved, to reverse what is, apparently, the natural order of things and to proceed from the more complex to the simpler—from highly complex objects of sense to successively simpler and simpler conceptual structures underlying these. Thus the order of quantitative determinations is: (1) Relative weights of comparable amounts of *matter in bulk* (gaseous or dissolved); (2) relative weights of *molecules*; (3) relative weights of *atoms*; and (4) if subsequent experiments should justify the most recent speculations, mass of *electrons*."

"The view here stated as to the true ratiocinative order of precedence of the molecular and atomic hypotheses has been held by various chemists; I have nowhere else seen it expounded with such wealth of illustration and with so extensive a knowledge of the fundamental literature of the subject as in the present monograph by Dr. Meldrum."

The pamphlet of 113 pages is divided into two parts. Part I. treats of the standing in chemistry of Avogadro's hypothesis, and Part II. of the standing in chemistry of Dalton's Atomic Theory.

The author is of the opinion that the services of Dalton have been overestimated. In one place he says: "In the composite man of science, to whom Roscoe gives the name of Dalton, it is easy to discern the features of Charles, Gay-Lussac and Lavoisier. Plainly, the effect of all this is to obscure the individuality of Dalton and in his interests, therefore, to justify and make indispensable an impartial inquiry into his merits."

A careful study of this book would help chemists, whether young or old, to see some of the fundamental problems of their science in a clearer light than usual. It is cordially recommended.
I. R.

LABORATORY STUDIES FOR BREWING STUDENTS. By ADRIAN J. BROWN. London and New York: Longmans, Green & Co. 1905. Price, $2.50.

The title of this volume suggests its purpose. It is designed for students of brewing who are under the guidance of an instructor. The laboratory directions, as a whole, are very helpful and those relating to chemical work represent the methods in vogue in England. Although this book should be of considerable value to a beginner in brewing studies, the methods advocated for the analyses of raw materials do not harmonize with American practice. The author is evidently unacquainted with several publications[1] dealing with acid starch conversions and the analyses of the resulting products. The reviewer, therefore, cannot endorse the processes given for such work. The presence of dextrins in glucose (syrup) is certainly of sufficient importance to brewing students to warrant inserting methods for its estimation, which, unfortunately, are omitted in this volume.

In addition to the chemical side of brewing materials, sufficient directions in elementary bacteriology and yeast culture are given, supplemented by convenient references to more elaborate works, for those who desire extended investigation in the lines indicated. GEORGE DEFREN.

THE NEW KNOWLEDGE. A Popular Account of the New Physics and the New Chemistry in Their Relation to the New Theory of Matter. By ROBERT KENNEDY DUNCAN, Professor of Chemistry in Washington and Jefferson College. Illustrated. New York: A. S. Barnes & Company. 1905. pp. 263. Price, $2.00 net.

The author has made a good selection of material for this book. It is written with enthusiasm. Indeed, this not infrequently is present in such excess as to lead dangerously near to the sensational. There is a lack of perspective in the work, due, in part, to the author's attitude toward the historical method, which he characterizes, in his preface, as "the death of clear exposition."

Any discussion of modern discoveries, which ignores what has been done in the past, is liable to value unduly the newest developments, and this is a serious defect in the present book. From this work, alone, one would conclude that most of the science of the last century was now obsolete. Indeed, it is stated in the preface that "where before there was solid walking ground to the older science now there is nothing but shifting sand." This is liable to leave an entirely erroneous impression, especially upon the popular mind.

Again, inaccuracy of statement is not infrequent. A few examples will make the above points clear.

That "the properties of ether are for the most part negative" (p. 3) or that "the doctrine of the conservation of energy is receiving some hard knocks nowadays" (p. 7) will scarcely receive the sanction of the leading physicists.

Similarly, the physical chemist will not be convinced, in speaking of positive ions, that "their electrical charge is of the same order as that of an ordinary atom" (p. 76), since atoms are uncharged. Further, the term "order," as here used, is ambiguous.

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[1] J. Am. Chem. Soc., **18**, 748, 869. [Revised in Technology Quarterly, **10**, 133]; *Ibid.*, **19**, 261; **25**, 1003.

The paragraph on valency (pp. 166–167) is without the proper perspective. We knew that "it was electrical in its origin" before the discovery of the "electron." That Faraday's Law is the basis of valency has been pointed out frequently by the reviewer and has been made the basis of the discussion of this subject in both his Physical and Inorganic Chemistries.

On p. 167 it is stated that "a univalent positive atom is one which, under the circumstances of chemical action, attains stability by losing one, and only one, corpuscle." This sentence contains an unusual number of errors. In the first place, an atom is always uncharged and is, therefore, neither positive nor negative. Evidently an ion is meant. Secondly, in terms of this statement, we should have valency only "under the circumstances of chemical action," which is meaningless. Thirdly, what is lost is not a "corpuscle" but an electron. The author fails, repeatedly, to distinguish between the two.

The statements about the formation of helium from the radium emanation and concerning the relations of alchemy to modern chemistry, could be advantageously revised.

It should have been pointed out that the positive particles, corresponding to the negative electrons, probably exist in the "canal or anode rays" discovered by Goldstein.

It appears, to the reviewer, that the style of the book would have been more dignified and more conclusive to cool, scientific thought, had such headings as the following been omitted, or at least revised: "*A New Use for Clouds,*" "*Discovery of the One Thing,*" "*Celestial Dissociation,*" "*The Reconstruction of a Universe,*" etc.

The author of this book has undoubtedly followed closely the recent developments in the physical sciences and his work is, for the most part, clear and interesting. It is unfortunate that it should contain such serious defects. H. C. J.

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CHEMICAL JOURNAL

A STUDY OF THE TEMPERATURE COEFFICIENTS OF CONDUCTIVITY IN AQUEOUS SOLUTIONS AND ON THE EFFECT OF TEMPERATURE ON DISSOCIATION.

BY HARRY C. JONES AND AUGUSTUS P. WEST.

INTRODUCTION.

It is now generally recognized that ions are the chief agents which bring about chemical action. The chemical activity of solutions is, then, a function of the dissociation of the dissolved substances. Since conductivity is a measure of dissociation, there is, therefore, a close relation between the conductivity of solutions and their chemical activity. The conductivities of a large number of substances in aqueous solutions have been determined at 18° and 25°, while at other temperatures not very much work has been done. It is well known, however, that the conductivity of solutions is greatly affected by temperature. Consequently, a study of the exact effect of temperature on the conductivity of aqueous solutions and on their dissociation, is of considerable importance, especially for those temperatures and dilutions more frequently employed in the determination of conductivity. The temperatures in question range from 0° to 35° and the dilutions from N/2 to N/1024.

Historical Review.

Quite a number of investigators have studied the effect of temperature on conductivity and some interesting results have been obtained, not only at intermediate temperatures, but at those below 0° and above 100°. It was very early observed that conductivity is affected by temperature. Ohm[1] noticed this fact in 1844 and two years later Hankel[2] made the same observation. The problem was not seriously considered, however, until some years afterwards, when Grotrian[3] took it up. He determined the conductivity of a few dilutions of sulphuric and hydrochloric acids, at various temperatures, and showed that the effect of temperature on conductivity, in the case of sulphuric acid, could be represented by an equation of the form

$$L = L_0 (1 + \alpha t + \beta t^2),$$

and in the case of hydrochloric acid the temperature effect could be represented by the formula

$$L = L_0 (1 + \alpha t).$$

In each of these formulas L represents the molecular conductivity, t is the temperature in question, and α and β are constants.

Kohlrausch and Grotrian,[4] a year later, studied the influence of temperature on conductivity. They worked out the temperature coefficients of a few acids and salts, and suggested that the effect of temperature on conductivity could be best represented by the formula which Grotrian had deduced for sulphuric acid.

Other investigators have determined temperature coefficients of conductivity but, in many cases, they studied only a few compounds at various dilutions.

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[1] Pogg. Ann., 63, 403 (1844).

[2] *Ibid*., 69, 255 (1846)

[3] *Ibid.*, 151, 378 (1874).

[4] *Ibid.*, 154, 224 (1875).

Krannhals[1] determined the conductivity of hydrochloric acid and a few inorganic salts, over a range of temperature extending from 18° to 100°. He found, as others before him had done, that conductivity increases with rise in temperature and with increase in dilution. He concluded from his results that temperature has no effect on dissociation. Rudolphi[2] made some conductivity measurements between 25° and 100°. His results also showed that temperature has practically no effect on dissociation. Jahn[3] determined the conductivity of a number of fatty acids between 10° aad 50°. He measured dilutions only as high as N/128, consequently, his dissociation values could not be very accurate. Others who have made conductivity measurements at different temperatures and calculated temperature coefficients, are Bouty,[4] Long[5] and Freund.[6]

Arrhenius,[7] in 1887, showed the connection between the lowering of the freezing-point of a solvent by an electrolyte and the conductivity of the electrolyte. In most of the earlier experiments, however, the values obtained for the amount of dissociation at 0°, by the freezing-point method, were generally a little higher than those obtained by the conductivity method at 18° and 25°. This would indicate that there is a small negative temperature coefficient of dissociation. Two years later Arrhenius[8] studied this problem. He worked out the temperature coefficients of conductivity of a number of salts, at various temperatures, ranging from 18° to 52°. His results showed that temperature has little or no effect on dissociation.

Déguisne[9] studied the effect of temperature on conductivity in very dilute, or completely dissociated solutions of strong electrolytes. He worked at various temperatures from 0° to 34° and expressed the influence of temperature, *t*, on the conductivity, K, starting from 18° as a mean temperature, in the form of the following equation:

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[1] Z. physik. Chem., **5**, 250 (1890).

[2] *Ibid.*, **17**, 385 (1895).

[3] *Ibid.*, **16**, 72 (1895).

[4] Ann. Chim. Phys., [6], **3**, 498 (1884).

[5] Wied. Ann., **11**, 37 (1880).

[6] *Ibid.*, **7**, 47 (1879).

[7] Z. physik. Chem., **1**, 631 (1887).

[8] *Ibid.*, **4**, 96 (1889).

[9] Dissertation, Strassburg (1895).

$$Kt = K_{18}\,(1 + \alpha(t-18) + \beta(t-18)^2).$$

R. W. Wood[1] measured the conductivity of several electrolytes in dilute solutions, at 0°. He calculated the dissociation at 0° and compared his values with those obtained by Kohlrausch at 18°. He found, as others had done before him, that, in dilute solutions, temperature has practically no effect on dissociation.

Schaller[2] made conductivity measurements of several electrolytes in dilute solutions, at various temperatures between 25° and 100°. In order to avoid the action of water on glass at high temperatures, he employed a platinum vessel, but it was found that in the case of acids and neutral salts, vessels made of Jena glass might be used. The conductivity was found to increase with rise in temperature, but at a diminishing rate. The dissociation was found to decrease with rise in temperature. Schaller, however, did not work at temperatures as low as 0°, so that the exact effect of temperature on dissociation, for temperatures ranging from 0° to 25°, was still an unsettled question.

Whetham[3] carried out a very careful piece of conductivity work at 0°, for the purpose of comparing the dissociation values thus obtained, with those worked out by the freezing-point method a little below 0° and also with the values obtained by Kohlrausch at 18°, using the conductivity method. He worked with several electrolytes and found that dissociation decreased very slightly with rise in temperature.

Douglas[4] studied the effect of temperature on the conductivity of a number of electrolytes. He worked with several acids, bases and salts at various temperatures, ranging from

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[1] Phil. Mag., **41**, 117 (1896).

[2] Z. physik. Chem., **25**, 497 (1898).

[3] Phil. Trans., **194**, 321 (1900).

[4] THIS JOURNAL, **26**, 428 (1901).

0°–35°. His results indicate that temperature has practically no effect on dissociation.

As we have seen, Whetham's results obtained the year before indicated that there was a very slight decrease in dissociation with rise in temperature. Thus the problem as to the exact effect of temperature on dissociation, over a range of temperature extending, say, from 0°–35°, was still an unsettled one. Some important investigations have been carried out at temperatures below 0° and above 35°, and some interesting results have been obtained.

Kohlrausch[1] pointed out that it was probable that the conductivities of all aqueous solutions approach, with decreasing temperature, a zero value at about the same temperature, which is —38°.5, and that the cause of this phenomenon is to be sought for in the disappearance of the fluidity of water at this temperature. In a later paper, Kohlrausch[2] showed that, if the conductivity curves of a number of electrolytes were extrapolated below 0°, in accordance with Déguisne's formula, they would all approach a zero value of conductivity at about —38°.5. He also pointed out the fact that, if the curves showing the relations between fluidity and temperature were extrapolated, they would also cut the zero axis at about the same point. That is, conductivity and fluidity disappear at the same point. Of course, wide extrapolation is necessary, and this fact must be taken into account. What is more significant, the conductivity curve for certain salts, notably sodium valerate, is almost identical with the fluidity curve, and further, the temperature coefficient of ionic mobility, in the case of slow moving ions, is almost the same as that of fluidity. In order to explain these facts and avoid the assumption that ionic motion is independent of the motion of the solvent, Kohlrausch proposed the hypothesis that about every ion there moves an atmosphere of the solvent, the dimensions of which are determined by the individual characteristics of the ion. The direct action between the ion and the solvent diminishes as the atmosphere becomes of greater dimensions. This hypothesis accounts for the apparent disappearance of fluidity and conductivity at the same temperature. The idea of ionic hydration was not entirely original with Kohlrausch. Ciamician,[1] some years before, had suggested that around every ion there is a shell of water. He also attempted, by diffusion methods, to measure the amount of this hydration.

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[1] Sitzun. Berlin, 1028 (1901).

[2] P. Roy. Soc., 71, 338 (1903).

Kunz,[2] at the suggestion of Kohlrausch, made some conductivity measurements on sulphuric acid at various temperatures, ranging from 0° to —70°. He worked with several solutions of various concentrations, from 19.1 to 63.76 per cent. His conductivity curves, representing conductivity as a function of temperature, do not meet the temperature axis at —38°.5, as Kohlrausch had predicted. Instead of the curves converging at one point, they approach the abscissa more and more slowly as the temperature falls. Kunz adopted the view that electrical resistance is due to friction. In a later article, Kunz[3] stated that he had obtained similar results with calcium chloride and sodium hydroxide. These results would seem to indicate that the hypothesis of Kohlrausch could not easily be demonstrated experimentally.

In an interesting article, W. R. Bousfield and T. M. Lowry[4] point out the effect of temperature on conductivity over a wide range of temperature. They show that conductivity-temperature curves cannot be represented by a linear or parabolic formula, as Kohlrausch has suggested. At high and low temperatures, no general formula will account for the facts. The conductivity-temperature curves, when plotted for a long range of temperature, are all inflected curves which contain a maximum point.

At low temperatures, the effect of temperature on conductivity is determined mainly by the changing mobility of the ions. At higher temperatures, the change in dissociation becomes a dominant factor and, just as the increasing viscosity of the solution leads at lower temperatures to a lower conductivity zero, at which the viscosity of the liquid would altogether prevent ionic mobility, so at higher temperatures an upper limit may exist, at which the conductivity would again become zero, owing to the complete disappearance of dissociation. The different behavior of acids and salts, which is unimportant in the case of the lower conductivity zero, becomes a vital factor in discussing the possible existence of an upper conductivity zero.

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[1] Z. physik. Chem., **6**, 403 (1890).

[2] Compt. rend., **135**, 788 (1902).

[3] Z. physik. Chem., **42**, 591 (1903).

[4] P. Roy. Soc., **51**, 467 (1902).

Armstrong[1] called attention to the fact that, while the majority of salts are conductors, *per se*, the acids are, in the pure state, dielectrics and only become electrolytes by interaction with a dissociating solvent. In virtue of their inherent power of self-ionization, the salts may, therefore, exhibit some conducting power, independent of that due to the dissociating properties of the solvent, while it is to be expected that the acids would cease to be electrolytes if the solvent, by reason of increasing temperature, should lose its power of dissociation. For this reason, evidence of the existence of an upper conductivity zero is to be looked for, in solutions of substances which, like the acids, are incapable of self-ionization.

Arrhenius[2] pointed out the effect of decreasing dissociation with rise in temperature, in the case of phosphoric and hypophosphoric acids, which exhibit maxima of conductivity at 54° and 75°, respectively. Sach[3] also observed this phenomenon in the case of aqueous solutions of copper sulphate. In the majority of cases the maximum of conductivity lies above the boiling-point, and experimental work is rendered very difficult, owing to the ready solubility of glass at high temperatures.

Miss Maltby[4] found that, on heating up to 237°, the conductivity of an aqueous solution of potassium chloride reached a maximum and decreased as the temperature rose. Hagenbach[5] observed a maximum in the conductivity of a 0.01 N solution of potassium chloride. In these experiments the conductivity cells were of glass, consequently the results were not very accurate. Noyes and Coolidge[6] studied the effect of temperature on the conductivity of aqueous solutions of sodium and potassium chlorides. They worked at various temperatures ranging from 140°–306°. At 280° the conductivity curves of both chlorides for 0.1 N solutions reach a maximum and then fall. They proved, in the case of a 0.5 N solution of the salts, that these maxima in the curves would probably be much more pronounced. Their results show that, at the higher temperatures, there is a marked decrease in dissociation. In their work they used a steel bomb lined with platinum, which would eliminate any error arising from the solubility of glass.

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[1] P. Roy. Soc., **40**, 268 (1886).

[2] Z. physik. Chem., **4**, 96 (1889).

[3] Wied. Ann., **43**, 212 (1891).

[4] Z. physik. Chem., **18**, 155 (1895).

[5] Ann. d. Phys., **5**, 276 (1901).

[6] Z. physik. Chem., **46**, 323 (1904). J. Am. Chem. Soc., **262**, 134 (1904).

There is more evidence available for the existence of conductivity-temperature curves containing maxima and perhaps an upper conductivity zero, as was pointed out by Messrs. Bousfield and Lowry, in the case of non-aqueous solvents. Franklin and Kraus[1] found that, at high temperatures, the conductivity of solutions in liquid ammonia decreases with rise in temperature. Miss Maltby[2] has shown that, even at atmospheric temperatures, the conductivity of an ethereal solution of hydrochloric acid decreases as the temperature rises. Cattaneos[3] obtained negative temperature coefficients in solutions in ether, alcohol and glycerol. Hagenbach[4] obtained maxima in the conductivity-temperature curves at about 120°, in solutions of several salts in liquid sulphur dioxide. Walden and Centnerzwer[5] determined the conductivity of hydrochloric acid and a number of organic compounds, dissolved in sulphur dioxide. The results with hydrochloric acid are especially interesting, because it is known to be of itself a non-electrolyte, and to possess no power of undergoing dissociation, unless brought in contact with a dissociating medium. At the critical temperature of the solvent, the conductivity decreased to a zero value, which is, therefore, identical with the upper conductivity zero of the solution. Kraus[6] investigated solutions of various electrolytes dissolved in methyl and ethyl alcohols.

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[1] This Journal, **24**, 83 (1900).

[2] Z. physik. Chem., **18**, 133 (1895).

[3] Rend. Lincei, [5]. **2**, 1. 295 (1893); *Ibid.*, [5], **2**, 2, 112 (1893).

[4] Ann. d. Phys., [5], **2**, 276 (1901).

[5] Z. physik. Chem, **39**, 549 (1902).

[6] Phys. Rev., **18**, 40 (1904).

He studied the conductivity up to, through and beyond the critical temperature of the solvents, and showed that the conductivity-temperature curve passes through a maximum with rise in temperature. The maximum in the case of solutions in methyl alcohol occurs at 150°, while in solutions of ethyl alcohol it is at 100°. In the case of solutions of potassium iodide, dissolved in methyl and ethyl alcohols, the conductivities did not reach a zero value at the critical temperature of the solvent. Although the resistance attained considerable magnitude, the solutions still remained conductors beyond the critical temperature. Since potassium iodide is an electrolyte *per se*, this is what we would expect, according to the idea advanced by Bousfield and Lowry. Although these interesting results point to the probable correctness of the Bousfield-Lowry hypothesis, concerning the effect of temperature on the conductivity of acids and salts, nevertheless, we may fairly question whether there is enough experimental evidence to justify any general conclusion. However, there is, undoubtedly, sufficient evidence to support the idea that the effect of temperature on conductivity, over a wide range of temperature, can only be represented by inflected conductivity-temperature curves, which contain a maximum point.

The most important point in the paper of Bousfield and Lowry and one that has been generally overlooked, is the fact that the normal form of the conductivity-temperature curve, for a composite electrolyte, is an inflected curve which contains a maximum. A wide-spread impression exists, however, that an inflection in the conductivity-temperature curve indicates some abnormal change in the character of the solution. This impression has been strengthened, if indeed it has not been created, by the general adoption of a linear or parabolic formula to express the influence of temperature on conductivity. Kohlrausch makes no reference to the existence of inflected curves which contain a maximum point. Trotsch,[1] who observed inflections in the case of a number of sulphates and chlorides of copper and cobalt, regarded them as due to the decomposition of hydrates existing in the solution.

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[1] Ann. d. Phys. [3], **41**, 259 (1890).

Purpose of this Investigation.

Having given a brief review of what has been done on the effect of temperature on dissociation, conductivity and the temperature coefficient of conductivity, we shall now take up the work, the results of which are recorded in this paper. It is well known that different types of compounds show different degrees of dissociation and, as we have seen, the exact effect of temperature on dissociation, over the ordinary range of temperature, say from 0°–35°, has not, as yet, been fully established for any considerable number of substances. This particular problem, including its connection with other important researches along this same line, together with various hypotheses which have been proposed in recent years, is the object of this investigation. The temperature coefficients of conductivity, expressed in percentage of conductivity units, have also been worked out according to the Kohlrausch formula, and the effect of temperature on these temperature coefficients has been studied. In addition to this, the temperature coefficients, expressed in conductivity units, or increments of conductivity with rise in temperature, have been calculated and the effect of temperature on these increments has been investigated.

EXPERIMENTAL PART.

Apparatus.

The Kohlrausch method of measuring conductivity was used throughout this investigation. The bridge-wire was of "manganin" and was calibrated by the method of Strouhal and Barus.[1]

The resistance coils were standardized and found to be accurate to within 0.04 per cent.

The conductivity cells were of the form used by Jones and Lindsay.[2] They differed from the ordinary Arrhenius cells in that they were provided with a ground-glass stopper to prevent evaporation. The electrodes were cut from thick sheet platinum, and into each circular plate a stout platinum wire, about an inch in length, was welded. Glass tubes were sealed on to the platinum wires and electrode plates by means of sealing glass. The electrodes were then treated in the manner recommended by Whetham.[1] They were first coated with platinum black in the usual manner, and afterwards heated to a high temperature in the flame of a blast-lamp. Electrodes coated with platinum black have the property of absorbing a small amount of salt from the solution and of giving some of it up again when water, or a more dilute solution, is placed in the cell. The investigation of very dilute solutions is thus rendered less accurate. The heating process gives a gray surface, which does not absorb any appreciable quantity of salt. The oxidizing action of the platinum black is also avoided by this treatment.

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[1] Wied. Ann., **10**, 326 (1880).

[2] This Journal, **28**, 329 (1902).

The tubes carrying the electrodes, thus treated, were forced through thin rubber tubing and inserted into the glass tubes in the cell cap. Hot sealing-wax was then carefully poured over the joint, on the outside of the cap. The cell constants were determined by means of solutions of potassium chloride having a concentration 0.02 N for cells designed for concentrated solutions; for cells intended for dilute solutions a 0.002 N solution of potassium chloride was employed. Each cell was adjusted for a particular range of dilution. The adjustment was made by raising or lowering the electrodes, having first heated the sealing-wax on the cap. When the cells were finally adjusted the constants were carefully redetermined.

The determination of the cell constants was carried out in a manner somewhat different from that ordinarily employed. When a cell containing a solution is placed in a thermostat, at 25°, and allowed to come to constant temperature, air-bubbles collect around the electrodes. It is difficult to dislodge the bubbles without changing the temperature of the solution somewhat. By moving the electrodes the bubbles can be dislodged, but some minutes must elapse in order to establish temperature equilibrium before readings can be made. In the meantime more bubbles may have collected. This difficulty was avoided by first placing the cells in a zero-bath and allowing them to remain there about a quarter of an hour. They were then removed to the thermostat-bath at 25° and allowed to remain nearly an hour. By this mode of procedure no bubbles, or at least only a very few, collected on the electrodes. After the readings were taken the cells were allowed to remain a quarter of an hour longer, and duplicate readings were made. The second readings were nearly always identical with the first, within the limit of error of reading. The following day the whole process was repeated. With careful manipulation, cells calibrated in this manner give very accurate results and the variation in the cell constants, produced by continual use, is very small. The constants were, however, redetermined every few weeks, since small particles of platinum are liable to be removed by abrasion.

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[1] Phil. Trans., **94**, [A], 321 (1900).

Four thermostats were used in this work, for the various temperatures ranging from 0°–35°. The zero-bath was of the type used by Jones and Lindsay,[1] though somewhat larger. It consisted of an outer and inner vessel. The inner vessel and the annular space between the two were filled with finely crushed ice. The outer portion of ice was moistened with a small quantity of distilled water, and to the ice in the inner vessel a larger amount of distilled water was added. The inner vessel contained a shelf for supporting the cells. Cells immersed in such a bath could be kept for any desired period at 0°.02–0°.05. The bath for the temperature next above zero was prepared in the following manner: A constant stream of hydrant water was passed through a large vessel, the water, being admitted at the bottom and allowed to flow out at the top, was kept thoroughly stirred by means of a small, hot-air engine. After running about an hour the temperature of the water remained almost constant. A small flame was now placed under the bath and by proper adjustment of this and of the rate of flow of the tap water, a constant temperature could be easily maintained. The 25° and 35° baths were obtained in the ordinary way and were stirred by hot-air engines. The Ostwald thermo-regulator was used and the temperature remained constant to 0°.005. The thermometers employed could be accurately read to 0°.02. The burettes and measuring flasks were carefully calibrated for 20°, according to the method of Morse and Blalock.[1]

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[1] This Journal, 28, 329 (1902).

Preparation of the Solutions.

In the preparation of the solutions, Kahlbaum's purest materials were invariably employed. These were, however, always tested for any possible impurities, which were removed. In some cases the standardization was effected by simply weighing the substance. When this was not possible the solutions were standardized by analysis. In making up a series of dilutions from the mother-solution of any substance, the temperature was, of course, kept under control and usually to within 0°.5 of the calibration temperature of the burettes and measuring flasks. The various concentrations were obtained by successive dilution, the mother-solution being the starting-point.

The water used in preparing the solutions was purified according to the method of Jones and Mackay.[2] Ordinary distilled water, after the addition of potassium bichromate and sulphuric acid, was redistilled. The distillate was distilled from acidified potassium bichromate and then, finally, from barium hydroxide. Water purified by this method gives a conductivity, at 25°, varying from 1.5 to 2.0×10^{-6}. The water correction, which must be applied to the values of the molecular conductivity at a given dilution (μ_v), usually does not attain an appreciable value until a dilution of about N/512 is reached.

Conductivity Measurements.

In making the conductivity measurements, from three to five different resistances were used for every solution. The values for the molecular conductivity (μ_v), given in the tables, are, therefore, the mean of several determinations.

Experimental Results.

In discussing the experimental results, the first substance considered is ammonium chloride. As the numerical results given in each table on ammonium chloride are of considerable interest in connection with certain theoretical ideas which have been advanced in recent years, the data given in each table will be discussed separately. After a full discussion of the results with ammonium chloride, the results with the other electrolytes will be taken up in order and the data discussed collectively, because the results with the other electrolytes are of the same general character as those with ammonium chloride, except in the case of acids.

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[1] THIS JOURNAL, **16**, 479 (1894).

[2] *Ibid.*, **19**, 91 (1897).

Ammonium Chloride.

The pure salt was dried by heating in an air-bath, for several hours, at 120°, after which it was placed in a desiccator until used. In making up the solutions, the exact amount of the salt necessary to make a 0.05 N solution was weighed out and introduced into a measuring flask.

Table I.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.5.	μ_v 25°.	μ_v 35°.
2	62.76	89.86	109.2	129.9
8	66.17	96.11	118.6	142.8
16	68.02	99.26	123.2	148.2
32	70.2	102.4	127.6	153.7
128	73.08	107.6	133.4	161.4
512	74.39	109.8	136.8	165.4
1024	74.84	110.5	137.8	167.2

In Table I. are given the values of the molecular conductivities of the various solutions of ammonium chloride at the different temperatures; v is the volume of the solution which contains a gram-molecular weight of the electrolyte and μ is the molecular conductivity at the temperature in question. The molecular conductivity increases, of course, with rise in temperature and with increase in the dilution of the solution.

Table II.—Comparisons with the Work of Kohlrausch.

	Kohlrausch.	Calculated from our work.
v.	μ_v 18°.	μ_v 18°.
2	94.8	96.3
8	...	103.6
10	103.5	...
16	...	107.2
20	107.8	...
32	...	110.8
33.3	110.1	...
100	114.2	...
128	...	116.2
500	118.0	...
512	...	118.8
1000	119.0	...
1024	...	119.6
1667	119.7	...

In Table II. is given a comparison of our results with those of Kohlrausch. The experimental results were obtained by Kohlrausch at 18°. Our work was not done at 18°. However, by applying our temperature coefficients, either in conductivity units or percentage, we can easily calculate our experimental results over to the temperature 18° and thus make comparisons with the experimental values of Kohlrausch. It is apparent, from the values given in the table, that there is a very close agreement between the two sets of results. In certain cases, where the dilutions are nearly the same, the figures are almost identical. Wherever such comparisons are made, the columns headed "calculated" are from our own results.

Table III.—Temperature Coefficients in Conductivity Units.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	1.87	1.84	2.07
8	2.06	2.14	2.42
16	2.15	2.28	2.50
32	2.22	2.40	2.61
128	2.38	2.46	2.80
512	2.44	2.57	2.86
1024	2.46	2.60	2.94

Table III. gives the values of the temperature coefficients of conductivity expressed in conductivity units. They are calculated from the formula

$$\frac{\mu_v t_2 - \mu_v t_1}{t_2 - t_1} = \text{coefficient.}$$

Where μ_v represents the molecular conductivity, t_2 is the higher temperature and t_1 the lower temperature. The figures given are really increments of conductivity with rise in temperature. *The increments increase with rise in temperature and increase in dilution. This is always the case with salts*, while with acids, as we shall see, the increments increase with dilution, but decrease with rise in temperature. It is hardly necessary to point out the fact that these temperature coefficients are useful in calculating the conductivity of a solution of ammonium chloride at one temperature from the known conductivity at another temperature. By the aid of these temperature coefficients we can calculate conductivity values somewhat more readily than by the percentage temperature coefficients usually employed.

Table IV.—Temperature Coefficients in Per Cent.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	2.98	2.05	1.90
8	3.11	2.23	2.02
16	3.16	2.30	2.02
32	3.16	2.34	2.04
128	3.26	2.29	2.10
512	3.29	2.34	2.09
1024	3.29	2.35	2.13

In this table the temperature coefficients of conductivity, expressed in percentage of conductivity units, are given. They are calculated according to the well-known Kohlrausch formula, expressed in the symbols used by Ostwald and others and multiplied by 100. The formula, as it was applied, is

$$\frac{\mu_v t_2 - \mu_v t_1}{t_2 - t_1} \cdot \frac{1}{\mu_v t_1} \times 100.$$

Where μ_v represents the molecular conductivity, t_2 is the higher and t_1 the lower temperature. The figures show that *the percentage temperature coefficients decrease with rise in temperature. The molecular conductivity increases with rise in temperature,* as was shown by Table I., but the *percentage of increase decreases.* This fact is especially interesting when considered in connection with the next table.

Table V.—Percentage Dissociation.

v.	α 0°.	α 14°.5.	α 25°.	α 35°.
2	84.0	81.3	79.2	77.7
8	88.4	87.0	86.1	85.4
16	90.8	89.8	89.4	88.6
32	93.8	92.7	92.6	91.9
128	97.6	97.4	96.8	96.5
512	99.4	99.4	99.3	98.9
1024	100.0	100.0	100.0	100.0

Table V. gives the values of α, the percentage of dissociation, of ammonium chloride at the various temperatures for the different dilutions. α is calculated from the formula

$$\alpha = \frac{\mu_v}{\mu\infty} \times 100,$$

where μ_v represents the molecular conductivity and $\mu\infty$ the molecular conductivity at complete dissociation. In this case

$$\mu\infty = \mu_v \text{ at } 1024 \text{ liters.}$$

It is apparent, from the table, that *the percentage of dissociation decreases with rise in temperature.* As the temperature increases from 0° to 35°, the values of α decrease, except in the most dilute solutions, where the salt is completely, or almost completely dissociated. Of course, here we should not expect to notice a large decrease, except over a wide range of temperature.

Ammonium Bromide.

The pure salt was heated in an air-bath, for several hours, at 120°, after which it was dried in a desiccator for some days. The mother-solution was prepared by direct weighing; the other solutions were made by diluting the original one. As is shown by the numerical values given in the tables, the same kind of results are obtained with ammonium bromide as with ammonium chloride. In Table VI. the molecular conductivities are seen to increase with rise in temperature. Table VII. shows that the temperature coefficients of conductivity, expressed in conductivity units, increase with temperature. In Table VIII. the percentage temperature coefficients of conductivity decrease with rise in temperature, and Table IX. shows a decrease in dissociation with rise in temperature.

No table is given for ammonium bromide, which shows how our values of the molecular conductivities, calculated by means of the temperature coefficients, compare with those obtained experimentally by other investigators. It was not considered necessary in each case to include these tables, as a few will suffice to show the general agreement.

Table VI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 35°.
2	67.26	89.81	115.1	136.7
8	69.36	95.44	123.6	146.8
16	71.53	98.06	127.4	153.3
32	73.50	101.1	131.7	158.0
128	76.18	105.5	137.9	165.0
512	77.55	107.8	141.3	168.9
1024	77.06	107.5	140.9	169.5

Table VII.—Temperature Coefficients in Conductivity Units.

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	1.80	2.02	2.16
8	2.09	2.25	2.32
16	2.12	2.35	2.59
32	2.21	2.45	2.63
128	2.35	2.59	2.71
512	2.42	2.68	2.76
1024	2.43	2.67	2.86

Table VIII.—*Temperature Coefficients in Per Cent.*

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	2.68	2.25	1.88
8	3.01	2.36	1.88
16	2.96	2.40	2.03
32	3.01	2.42	2.00
128	3.08	2.46	1.98
512	3.12	2.49	1.95
1024	3.16	2.49	2.03

Table IX.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
2	87.3	83.5	81.7	80.6
8	90.0	88.8	87.7	86.6
16	92.8	91.2	90.4	90.4
32	95.4	94.1	93.5	93.2
128	98.9	98.1	97.9	97.3
512	100.0	100.0	100.0	99.6
1024	100.0	100.0	100.0	100.0

Sodium Bromide.

The salt was dried by heating for several hours, at 120°, after which it was placed in a desiccator until used. The mother-solution was made up by direct weighing and the other solutions obtained by dilution. Conductivity measurements were made at only three different temperatures. However, results of the same character were obtained as with the preceding salts. Ostwald has measured the conductivities of a few dilutions of sodium bromide, at 25°. His results are included in Table X. A comparison of the two series of results shows a close agreement.

Table X.—Molecular Conductivities.

				Ostwald.
v.	μ_v 0°.	μ_v 11°.8.	μ_v 25°.	μ_v 25°.
2	51.46	69.24	91.9	...
8	55.36	75.26	100.3	...
16	57.35	78.17	105.1	...
32	58.79	80.03	107.7	107.9
128	61.23	84.35	113.3	113.8
512	63.02	87.17	116.8	118.6
2048	64.48	89.34	121.1	119.9

Table XI.—Temperature Coefficients in Conductivity Units.

v.	0°–11°.8.	11°.8–25°.
2	1.50	1.72
8	1.69	1.90
16	1.76	2.04
32	1.80	2.10
128	1.96	2.19
512	2.04	2.24
2048	2.11	2.40

Table XII.—Temperature Coefficients in Per Cent.

v.	0°–11°.8.	11°.8–25°.
2	2.91	2.48
8	3.05	2.52
16	3.07	2.61
32	3.06	2.62
128	3.20	2.60
512	3.24	2.57
2048	3.27	2.69

Table XIII.—Percentage Dissociation.

v.	α 0°.	α 11°.8.	α 25°.
2	79.8	77.5	75.9
8	85.9	84.2	82.8
16	88.9	87.5	86.8
32	91.2	89.6	88.9
128	95.0	94.4	93.6
512	97.7	97.6	96.4
2048	100.0	100.0	100.0

Sodium Iodide.

The salt was dried by heating, for some hours, at 120° and then placed in a desiccator until used. The original solution was made up by direct weighing and the other solutions by diluting. As is shown by the numerical values given in the tables, the effect of temperature on conductivity and dissociation is the same as with the other salts.

Table XIV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 16°.	μ_v 25°.	μ_v 35°.
2	51.90	77.22	92.73	111.6
8	55.26	83.52	100.4	121.6
16	57.03	86.36	104.2	125.8
32	58.62	89.02	107.4	130.6
128	60.97	93.20	112.5	136.8
512	61.81	94.91	114.7	139.3
1024	63.14	96.28	116.4	141.8
2048	64.51	98.4	119.1	144.5

Table XV.—Temperature Coefficients in Conductivity Units.

v.	0°–16°.	16°–25°.	25°–35°.
2	1.58	1.72	1.88
8	1.77	1.88	2.12
16	1.83	1.98	2.16
32	1.90	2.04	2.32
128	2.01	2.14	2.43
512	2.07	2.20	2.46
1024	2.07	2.24	2.54
2048	2.12	2.30	2.54

Table XVI.—Temperature Coefficients in Per Cent.

v.	0°–16°.	16°–25°.	25°–35°.
2	3.04	2.23	2.03
8	3.20	2.25	2.11
16	3.21	2.29	2.07
32	3.24	2.29	2.16
128	3.30	2.30	2.16
512	3.35	2.32	2.14
1024	3.28	2.33	2.18
2048	3.29	2.34	2.13

Table XVII.—Percentage Dissociation.

v.	α 0°.	α 16°.	α 25°.	α 35°.
2	80.5	78.5	77.9	77.2
8	85.7	84.9	84.3	84.2
16	88.4	87.8	87.5	87.1
32	90.9	90.5	90.2	90.4
128	94.5	94.7	94.5	94.7
512	95.8	96.5	96.3	96.4
1024	97.9	97.8	97.7	98.1
2048	100.0	100.0	100.0	100.0

Sodium Carbonate.

The salt was dried for some hours, at 120° and then kept in a desiccator until used. Conductivity measurements were made at only three temperatures. In Table XIX. is given a comparison of the results obtained by Kohlrausch at 18°, with the values of the molecular conductivities calculated by means of the temperature coefficients between 15°.3 and 25°. As is shown by the table, there is a close agreement between the two sets of results.

Table XVIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 15°.3.	μ_v 25°.
2	50.99	78.94	100.4
8	70.7	109.1	137.8
16	79.75	123.8	155.4
32	87.28	134.7	170.8
128	99.16	155.4	197.9
512	105.8	166.9	209.6
1024	110.8	173.9	218.1

Table XIX.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	85.4	84.91
4	102.0	. .
8	. .	117.09
16	. .	132.6
20	136.4	. .
32	. .	144.7
40	150.2	. .
128	. .	167.2
200	179.8	. .

Table XX.—Temperature Coefficients in Conductivity Units.

v.	0°–15°.3.	15°.3–25°.
2	1.83	2.21
8	2.51	2.96
16	2.88	3.26
32	3.10	3.72
128	3.67	4.38
512	3.99	4.40
1024	4.12	4.56

Table XXI.—Temperature Coefficients in Per Cent.

v.	0°–15°.3.	15°.3–25°.
2	3.59	2.80
8	3.55	2.71
16	3.61	2.64
32	3.55	2.77
128	3.70	2.82
512	3.77	2.64
1024	3.72	2.62

Table XXII.—Percentage Dissociation.

v.	α 0°.	α 15°.3.	α 25°.
2	46.0	45.4	46.0
8	63.8	62.7	63.2
16	72.0	71.2	71.3
32	78.8	77.5	78.3
128	89.5	89.4	90.7
512	95.5	95.9	96.1
1024	100.0	100.0	100.0

Sodium Acetate.

The sodium acetate used was a specimen of the fused salt, obtained from Kahlbaum. After purification it was dried in an air-bath, for several days, at 120°. This treatment was necessary to bring it to constant weight. The original solution was made up by weight. Results of the same general character were obtained with sodium acetate as with the other salts.

The temperature coefficients, in conductivity units, are small, as might be expected from the comparatively small conductivity of the salt.

Table XXIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.6.	μ_v 25°.	μ_v 35°.
2	28.39	41.93	54.86	67.06
8	34.30	50.73	66.25	81.09
16	36.37	53.86	70.17	86.01
32	38.11	56.59	73.81	90.55
128	40.41	60.22	78.32	96.43
512	41.21	61.63	80.14	99.34
1024	40.65	61.15	79.12	98.6
2048	41.28	61.97	80.14	99.4

Table XXIV.—Temperature Coefficients in Conductivity Units.

v.	0°–13°.6.	13°.6–25°.	25°–35°.
2	0.996	1.13	1.22
8	1.21	1.36	1.48
16	1.29	1.43	1.58
32	1.36	1.51	1.67
128	1.46	1.59	1.81
512	1.50	1.62	1.92
1024	1.51	1.58	1.95
2048	1.52	1.59	1.93

Table XXV.—Temperature Coefficients in Per Cent.

v.	0°–13°.6.	13°.6–25°.	25°–35°.
2	3.51	2.69	2.22
8	3.53	2.68	2.23
16	3.52	2.66	2.25
32	3.57	2.67	2.26
128	3.61	2.64	2.31
512	3.67	2.63	2.38
1024	3.71	2.58	2.46
2048	3.68	2.57	2.41

Table XXVI.—Percentage Dissociation.

v.	α 0°.	α 13°.6.	α 25°.	α 35°.
2	68.9	67.9	68.5	67.5
8	83.2	82.3	82.7	81.6
16	88.3	87.4	87.6	86.6
32	92.2	91.8	92.1	91.2
128	98.1	97.7	97.7	97.1
512	100.0	100.0	100.0	100.0

Potassium Chloride.

The salt was recrystallized 5 times. It was then dried for several days, in an air-bath, at 150° and afterwards preserved in a desiccator until used. Conductivity measurements were made at 5 different temperatures. In Table XXVIII., the calculated values of the molecular conductivities, at 18°, show a very close agreement with those obtained experimentally by Kohlrausch at the same temperature.

Table XXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 4°.3.	μ_v 15°.5.	μ_v 25°.	μ_v 35°.
2	62.96	70.09	91.09	109.5	130.8
8	66.47	74.48	98.24	118.6	142.5
16	68.4	76.95	101.5	122.9	147.7
32	70.27	78.95	104.9	126.8	152.5
128	73.0	82.25	109.4	132.4	159.9
512	74.24	83.59	111.9	135.5	163.0
1024	75.14	84.59	112.9	137.0	165.4

Table XXVIII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	95.8	95.9
8	...	103.6
10	104.7	...
16	...	107.0
20	108.3	...
32	...	110.7
33.3	110.7	...
100	114.7	...
128	...	115.5
500	118.5	...
512	...	118.1
1000	119.3	...
1024	...	119.3
1667	119.9	...

Table XXIX.—Temperature Coefficients in Conductivity Units.

v.	0°–4°.3.	4°.3–15°.5.	15°.5–25°.	25°–35°.
2	1.66	1.88	1.94	2.13
8	1.86	2.12	2.14	2.39
16	1.99	2.19	2.25	2.48
32	2.02	2.32	2.31	2.57
128	2.15	2.42	2.42	2.75
512	2.17	2.53	2.48	2.75
1024	2.20	2.53	2.54	2.84

Table XXX.—Temperature Coefficients in Per Cent.

v.	0°–4°.3.	4°.3–15°.5.	15°.5–25°.	25°–35°.
2	2.63	2.68	2.13	1.94
8	2.78	2.80	2.18	2.01
16	2.91	2.85	2.22	2.02
32	2.87	2.94	2.20	2.03
128	2.94	2.94	2.21	2.08
512	2.92	3.03	2.22	2.03
1024	2.93	2.99	2.25	2.07

Table XXXI.—Percentage Dissociation.

v.	α 0°.	α 4°.3.	α 15°.5.	α 25°.	α 35°.
2	83.8	82.9	80.7	79.9	79.0
8	88.5	88.0	87.0	86.6	86.2
16	91.0	91.0	89.9	89.7	89.3
32	93.5	93.3	92.0	92.6	92.2
128	97.2	97.2	96.9	96.6	96.7
512	98.8	98.8	99.1	98.9	98.5
1024	100.0	100.0	100.0	100.0	100.0

Potassium Bromide.

The sample of potassium bromide, which was used, was prepared in the same manner as the preceding salts. It was dried for some hours, in an air-bath, at 110° and then placed in a desiccator until used. In Table XXXIII. is given a comparison of our calculated results with those obtained experimentally by Krannhals, at 18°. The two series of values agree very closely. The same general rule holds for dissociation and temperature coefficients, as has been observed with the preceding compounds.

Table XXXII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.5.	μ_v 25°.	μ_v 35°.
2	65.82	93.21	114.4	136.2
8	68.01	98.45	121.3	145.6
16	70.1	101.7	125.2	150.5
32	71.84	104.6	128.8	154.6
128	74.79	109.0	134.5	162.0
512	75.73	111.3	137.6	165.5
1024	79.23	115.6	143.5	172.6

Table XXXIII.—Comparison with the Work of Krannhals.

v.	Krannhals. μ_v 18°.	Calculated. μ_v 18°.
2	98.2	100.3
8	105.7	106.1
16	110.0	109.5
32	113.0	112.7
128	117.0	117.5
256	118.8	...
512	...	120.1
1000	121.0	...
1024	...	124.9

Table XXXIV.—Temperature Coefficients in Conductivity Units.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	1.89	2.02	2.18
8	2.10	2.18	2.43
16	2.18	2.24	2.53
32	2.26	2.30	2.58
128	2.35	2.43	2.75
512	2.45	2.50	2.79
1024	2.51	2.66	2.91

Table XXXV.—Temperature Coefficients in Per Cent.

v.	0°–14°.5.	14°.5–25°.	25°–35°.
2	2.87	2.17	1.90
8	3.09	2.21	2.00
16	3.07	2.20	2.02
32	3.15	2.20	2.00
128	3.14	2.23	2.04
512	3.24	2.25	2.03
1024	3.17	2.30	2.03

Table XXXVI.—Percentage Dissociation.

v.	α 0°.	α 14°.5.	α 25°.	α 35°.
2	83.1	80.6	79.7	78.9
8	85.8	85.2	84.5	84.4
16	88.5	88.0	87.2	87.2
32	90.8	90.5	89.8	89.6
128	94.4	94.3	93.7	93.9
512	95.6	96.3	95.9	95.9
1024	100.0	100.0	100.0	100.0

Potassium Iodide.

The potassium iodide was dried for several hours, at 110°. The original solution was made up by direct weighing. In Table XXXVIII. the comparisons of our figures for the molecular conductivities with the work of others, show close agreement. In some cases where the dilutions are the same, or very nearly the same, the numerical values are almost identical.

Table XXXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.1.	μ_v 25°.	μ_v 35°.
2	65.78	83.88	112.8	133.7
8	68.45	88.18	120.7	144.5
16	70.17	90.51	124.5	148.4
32	71.90	93.32	128.0	153.0
128	74.41	96.67	133.7	160.2
512	76.35	98.91	137.3	165.9
1024	77.77	101.9	141.8	170.9
2048	79.2	104.9	147.2	177.2

Table XXXVIII.—Comparison with the Work of Others.

	Ostwald.		Kohlrausch.	Calculated.
v.	μ_v 25°.	v.	μ_v 18°.	μ_v 18°.
	...	2	99.7	99.2
	...	8	...	105.4
	...	10	106.9	...
32	128.5	16	...	108.5
128	135.4	20	110.2	...
512	139.6	32	...	111.7
1024	140.7	33.3	112.3	...
	...	128	...	116.3
	...	166.7	117.6	...
	...	500	119.7	...
	...	512	...	119.2
	...	1000	120.3	...
	...	1024	...	123.0

Table XXXIX.—Temperature Coefficients in Conductivity Units.

v.	0°–10°.1.	10°.1–25°.	25°–35°.
2	1.79	1.94	2.09
8	1.95	2.18	2.38
16	2.01	2.28	2.39
32	2.12	2.33	2.50
128	2.20	2.48	2.65
512	2.23	2.58	2.86
1024	2.39	2.68	2.91
2048	2.54	2.84	3.00

Table XL.—Temperature Coefficients in Per Cent.

v.	0°–10°.1.	10°.1–25°.	25°–35°.
2	2.72	2.31	1.85
8	2.84	2.47	1.97
16	2.86	2.52	1.92
32	2.95	2.50	1.95
128	2.96	2.57	1.98
512	2.92	2.61	2.08
1024	3.07	2.63	2.05
2048	3.21	2.71	2.04

Table XLI.—Percentage Dissociation.

v.	α 0°.	α 10°.1.	α 25°.	α 35°.
2	83.1	80.0	76.6	75.5
8	86.4	84.1	82.0	81.5
16	88.6	86.3	84.6	83.7
32	90.8	89.0	87.0	86.3
128	94.0	92.1	90.8	90.4
512	96.4	94.3	93.3	93.6
1024	98.2	97.1	96.3	96.4
2048	100.0	100.0	100.0	100.0

Potassium Nitrate.

The specimen of potassium nitrate used was dried for 2 days, at 110° and then placed in a desiccator until used. The mother-solution was standardized by direct weighing. The comparisons of the molecular conductivities given in Table XLIII. show that our calculated values are practically the mean of those obtained experimentally by Kohlrausch and Krannhals, except in the very dilute solutions, where our values agree closely with those obtained by Kohlrausch.

Table XLII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.	μ_v 25°.	μ_v 35°.
2	54.02	69.67	95.21	113.8
8	61.94	80.22	111.0	132.4
16	65.33	84.31	116.3	139.0
32	67.92	87.78	121.3	145.0
128	72.05	93.57	129.5	154.1
512	76.34	98.71	137.0	163.9
1024	76.31	99.8	139.6	166.7

Table XLIII.—Comparison with the Work of Others.

	Kohlrausch.	Calculated.	Krannhals.
v.	μ_v 18°.	μ_v 18°.	μ_v 18°.
2	83.9	83.3	83.1
8	...	96.6	95.6
10	103.7	...	...
16	...	101.4	100.3
20	106.7	...	...
32	...	105.7	104.3
100	114.0	...	...
128	...	112.7	109.3
500	118.0	...	...
512	...	119.2	...
1000	119.0	...	114.0
1024	...	121.1	...

Table XLIV.—Temperature Coefficients in Conductivity Units.

v.	0°–10°.	10°–25°.	25°–35°.
2	1.56	1.70	1.86
8	1.83	2.05	2.14
16	1.90	2.13	2.27
32	1.99	2.23	2.37
128	2.15	2.40	2.46
512	2.24	2.55	2.69
1024	2.35	2.65	2.71

Table XLV.—Temperature Coefficients in Per Cent.

v.	0°–10°.	10°–25°.	25°–35°.
2	2.89	2.44	1.95
8	2.95	2.56	1.93
16	2.91	2.53	1.91
32	2.93	2.54	1.95
128	2.98	2.56	1.82
512	2.93	2.58	1.96
1024	3.08	2.65	1.94

Table XLVI.—Percentage Dissociation.

v.	α 0°.	α 10°.	α 25°.	α 35°.
2	70.8	69.8	68.2	68.3
8	81.2	80.4	79.5	79.4
16	85.6	84.5	83.3	83.4
32	89.0	88.0	86.9	87.0
128	94.4	93.8	92.8	92.4
512	100.0	98.9	98.1	98.3
1024	100.0	100.0	100.0	100.0

Potassium Sulphate.

The specimen of salt used was dried for some hours, at 120° and then kept in a desiccator until used. The comparison of the molecular conductivities given in Table XLVIII. are not quite as close as in the case of certain other salts.

The temperature coefficients in conductivity units are large and the conductivity of the salt itself is comparatively large.

Table XLVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 9°.5.	μ_v 25°.	μ_v 35°.
2	87.19	110.1	152.6	180.7
8	101.9	130.5	183.6	219.8
16	109.9	140.9	199.2	238.4
32	117.9	151.5	214.4	256.9
128	131.9	170.3	242.1	291.0
512	142.7	184.0	263.5	318.4
1024	145.0	187.0	268.0	325.0

Table XLVIII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	134.4	133.4
4	147.2	...
8	...	159.6
16	...	172.9
20	179.4	...
32	...	186.0
40	191.8	...
128	...	209.7
200	219.6	...
512	...	227.6
1000	236.2	...
1024	...	231.4
2000	241.4	...

Table XLIX.—Temperature Coefficients in Conductivity Units.

v.	0°-9°.5.	9°.5-25°.	25°-35°.
2	2.41	2.74	2.81
8	3.01	3.43	3.62
16	3.26	3.76	3.92
32	3.54	4.06	4.25
128	4.04	4.63	4.89
512	4.35	5.13	5.49
1024	4.42	5.23	5.70

Table L.—Temperature Coefficients in Per Cent.

v.	0°-9°.5.	9°.5-25°.	25°-35°.
2	2.76	2.49	1.84
8	2.95	2.63	1.91
16	2.97	2.67	1.97
32	3.00	2.61	1.98
128	3.06	2.72	2.03
512	3.05	2.79	2.08
1024	3.05	2.79	2.13

Table LI.—Percentage Dissociation.

v.	α 0°.	α 9°.5.	α 25°.	α 35°.
2	60.1	58.9	56.9	55.6
8	70.3	69.8	68.5	67.6
16	75.8	75.4	74.3	73.4
32	81.3	81.0	80.0	79.1
128	91.0	91.0	90.3	89.5
512	98.4	98.4	98.3	98.0
1024	100.0	100.0	100.0	100.0

Potassium Bisulphate.

The sample of salt was dried for several hours, at 110° and preserved in a desiccator until used. The original solution was made up by direct weighing. Here, again, we find the same phenomena that have appeared in the preceding cases; the percentage temperature coefficients of conductivity and the percentage dissociation decrease with rise in temperature.

The temperature coefficients in conductivity units are very large and the conductivity of the salt itself is very large, because it is an acid salt and splits off the swift hydrogen ion.

Table LII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 35°.
2	153.8	184.0	207.6	220.6
8	182.1	222.9	254.2	274.1
16	201.2	248.8	286.6	310.0
32	223.6	280.7	323.7	353.1
128	263.1	336.9	401.0	446.4
512	291.8	383.9	467.1	531.0
2048	290.9	385.8	478.2	556.6
8192	291.2	401.0	496.0	569.0

Table LIII.—Temperature Coefficients in Conductivity Units.

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	2.42	1.89	1.30
8	3.82	2.50	1.99
16	3.81	3.02	2.34
32	4.57	3.44	2.94
128	5.90	5.13	4.54
512	7.37	6.66	6.39
2048	7.59	7.39	7.84
8192	8.78	7.60	7.30

Table LIV.—Temperature Coefficients in Per Cent.

v.	0°–12°.5.	12°.5–25°.	25°–35°.
2	1.57	1.03	0.63
8	2.10	1.12	0.78
16	1.89	1.21	0.82
32	2.04	1.23	0.91
128	2.24	1.52	1.13
512	3.21	1.73	1.37
2048	2.61	1.92	1.64
8192	3.01	1.89	1.47

Table LV.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
2	52.8	45.9	41.9	38.8
8	62.5	55.6	51.3	48.2
16	69.1	62.0	57.8	54.5
32	76.8	70.0	65.3	62.1
128	90.3	84.0	80.8	78.5
512	100.0	95.7	94.2	93.3
2048	100.0	96.2	96.4	97.6
8192	100.0	100.0	100.0	100.0

Potassium Carbonate.

The salt was dried, for some hours, at 110°. The solutions were made up by direct weighing and dilution. The comparisons given in Table LVII. are not quite so concordant as in preceding cases. The conductivity measurements were made at only 3 temperatures.

Table LVI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 17°.8.	μ_v 25°.
2	84.34	129.2	150.1
8	98.74	154.1	180.9
16	105.3	166.5	195.3
32	112.9	179.6	210.5
128	122.3	197.6	233.6
512	131.2	211.1	250.1

Table LVII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	132.0	129.8
4	145.6	...
8	...	154.8
16	...	167.3
20	175.8	...
32	...	180.5
40	188.4	...
512	...	212.2
1000	239.8	...

Table LVIII.—Temperature Coefficients in Conductivity Units.

v.	0°–17°.8.	17°.8–25°.
2	2.52	2.90
8	3.11	3.72
16	3.44	4.00
32	3.75	4.29
128	4.23	5.00
512	4.49	5.42

Table LIX.—Temperature Coefficients in Per Cent.

v.	0°-17°.8.	17°.8-25°.
2	2.99	2.24
8	3.15	2.41
16	3.26	2.40
32	3.32	2.39
128	3.46	2.53
512	3.42	2.57

Table LX.—Percentage Dissociation.

v.	α 0°.	α 17°.8.	α 25°.
2	64.3	61.2	60.0
8	75.3	73.0	72.3
16	80.3	78.9	78.1
32	86.0	85.1	84.2
128	93.2	93.6	93.4
512	100.0	100.0	100.0

Potassium Ferrocyanide.

The sample of potassium ferrocyanide used was purified by repeated crystallization. The mother-solution was made up by direct weighing and the others obtained by dilution. In this case the effect of temperature on dissociation is very slight. The dissociation at 35° is 2 per cent less than at 0°, in a 0.25 N solution, showing a small, but distinct temperature effect in the more concentrated solutions. As we have seen, the decrease in dissociation with rise in temperature becomes greater as the concentration of the solution is increased. This salt is, therefore, no exception to the rule.

The temperature coefficients in conductivity units are the largest thus far met with, and the conductivity of the salt is very great, on account of the large number of ions into which it dissociates. The values of μ_v that are taken as $\mu\infty$ are probably somewhat too small, but they are the best that can be obtained in the circumstances.[1]

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[1] Jones and Bassett : THIS JOURNAL, 34, 313 (1905).

Table LXI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.1.	μ_v 25°.	μ_v 35°.
4	162.1	224.1	287.1	341.8
8	168.8	236.8	305.1	364.5
16	179.9	255.0	327.1	394.1
32	195.6	277.0	357.8	430.7
128	236.1	335.5	432.8	523.8
512	280.7	399.4	516.6	627.0
1024	295.1	421.4	546.5	660.0
2048	315.0	449.0	578.0	703.0
8192	328.0	467.0	599.0	724.0

Table LXII.—Temperature Coefficients in Conductivity Units.

v.	0°–13°.1.	13°.1–25°.	25°–35°.
4	4.73	5.29	5.47
8	5.19	5.74	5.94
16	5.73	6.06	6.70
32	6.21	6.79	7.29
128	7.59	8.18	9.10
512	9.06	9.85	11.04
1024	9.64	10.51	11.35
2048	10.23	10.84	12.50
8192	10.61	11.09	12.50

Table LXIII.—Temperature Coefficients in Per Cent.

v.	0°–13°.1.	13°.1–25°.	25°–35°.
4	2.91	2.36	1.91
8	3.08	2.42	1.62
16	3.19	2.38	2.05
32	3.17	2.45	2.04
128	3.21	2.44	2.10
512	3.22	2.47	2.14
1024	3.27	2.49	2.08
2048	3.24	2.41	2.16
8192	3.23	2.37	2.09

Table LXIV.—Percentage Dissociation.

v.	α 0°.	α 13°.1.	α 25°.	α 35°.
4	49.4	48.0	47.9	47.2
8	51.5	50.7	50.9	50.3
16	54.8	54.6	54.6	54.4
32	59.6	59.3	59.7	59.5
128	72.0	71.8	72.3	72.3
512	85.6	85.5	86.2	86.6
1024	90.0	90.2	91.2	91.2
2048	96.0	96.1	96.4	97.1
8192	100.0	100.0	100.0	100.0

Calcium Chloride.

The salt was dissolved in water and the strength of the solution determined by analysis, the calcium being weighed as calcium sulphate.

The temperature coefficients, in conductivity units, are large, as is the conductivity of the salt itself. The salt may show slight hydrolysis, which would affect the value of $\mu\infty$.

Table LXV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 11°.5.	μ_v 25°.	μ_v 35°.
2	89.32	119.7	159.2	190.3
8	105.5	147.8	193.4	233.8
16	112.3	157.5	207.4	250.1
32	118.5	163.4	219.9	266.0
128	129.9	179.8	243.6	295.0
512	138.2	192.1	260.8	316.4
1024	137.8	191.8	261.2	317.3

Table LXVI.—Temperature Coefficients in Conductivity Units.

v.	0°–11°.5.	11°.5–25°.	25°–35°.
2	2.64	2.93	3.11
8	3.68	3.38	4.04
16	3.93	3.70	4.27
32	3.90	4.18	4.61
128	4.34	4.73	5.14
512	4.69	5.09	5.56
1024	4.70	5.14	5.61

Table LXVII.—Temperature Coefficients in Per Cent.

v.	0°–11°.5.	11°.5–25°.	25°–35°.
2	2.96	2.45	1.95
8	3.49	2.29	2.09
16	3.50	2.33	2.06
32	3.29	2.56	2.10
128	3.34	2.63	2.11
512	3.39	2.65	2.13
1024	3.41	2.68	2.15

Table LXVIII.—Percentage Dissociation.

v.	α 0°.	α 11°.5.	α 25°.	α 35°.
2	64.8	62.4	60.9	60.0
8	76.6	77.1	74.0	73.7
16	81.5	82.1	79.4	78.8
32	85.9	85.1	84.2	83.8
128	94.3	93.7	93.3	93.0
512	100.0	100.0	99.8	99.7
1024	100.0	100.0	100.0	100.0

Calcium Bromide.

The mother-solution of calcium bromide was standardized by analysis. The calcium was determined as the sulphate. We have, in this case, the same general temperature effect as that already noted for other substances. The percentage temperature coefficients of conductivity and the percentage dissociation decrease with rise in temperature.

The same remarks apply to the temperature coefficients in conductivity units and to the conductivity itself, as in the case of calcium chloride.

Table LXIX.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.4.	μ_v 25°.	μ_v 35°.
2	85.95	122.7	151.0	181.1
8	97.74	144.0	177.5	214.8
16	103.0	150.5	188.4	227.6
32	108.2	158.4	199.0	240.5
128	117.3	173.3	217.9	265.0
512	122.9	182.0	229.7	278.5
1024	126.3	186.9	236.5	286.5
2048	126.8	188.2	239.5	291.5

Table LXX.—Temperature Coefficients in Conductivity Units.

v.	0°–14°.4.	14°.4–25°.	25°–35°.
2	2.55	2.67	3.01
8	3.21	3.16	3.73
16	3.30	3.58	3.92
32	3.49	3.83	4.15
128	3.89	4.21	4.71
512	4.10	4.50	4.88
1024	4.21	4.68	5.00
2048	4.26	4.84	5.20

Table LXXI.—Temperature Coefficients in Per Cent.

v.	0°–14°.4.	14°.4–25°.	25°–35°.
2	2.97	2.18	1.99
8	3.28	2.19	2.10
16	3.20	2.37	2.08
32	3.23	2.42	2.09
128	3.32	2.43	2.16
512	3.34	2.47	2.13
1024	3.33	2.50	2.11
2048	3.36	2.57	2.17

Table LXXII.—Percentage Dissociation.

v.	α 0°.	α 14°.4.	α 25°.	α 35°.
2	67.7	65.2	63.1	62.1
8	77.1	76.5	74.1	73.7
16	81.2	80.0	78.7	78.1
32	85.3	84.2	83.1	82.5
128	92.5	92.1	91.0	90.9
512	96.9	96.7	95.9	95.5
1024	99.6	99.3	98.7	98.3
2048	100.0	100.0	100.0	100.0

Strontium Bromide.

The strength of the original solution was determined by analysis, the strontium being weighed as the sulphate.

Table LXXIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.5.	μ_v 25°.	μ_v 35°.
2	88.03	122.1	153.8	183.1
8	100.0	141.8	180.6	217.2
16	103.7	148.1	190.0	228.1
32	110.0	157.2	202.2	243.9
128	117.8	170.6	219.1	267.1
512	128.8	185.4	239.1	289.9
1024	129.1	186.6	239.6	292.3

Table LXXIV.—Temperature Coefficients in Conductivity Units.

v.	0°–13°.5.	13°.5–25°.	25°–35°.
2	2.52	2.76	2.93
8	3.10	3.37	3.66
16	3.29	3.64	3.81
32	3.50	3.91	4.17
128	3.91	4.22	4.80
512	4.19	4.67	5.08
1024	4.26	4.61	5.27

Table LXXV.—Temperature Coefficients in Per Cent.

v.	0°–13°.5.	13°.5–25°.	25°–35°.
2	2.86	2.26	1.91
8	3.10	2.38	2.03
16	3.17	2.46	2.01
32	3.18	2.49	2.06
128	3.32	2.17	2.19
512	3.25	2.52	2.13
1024	3.30	2.47	2.20

Table LXXVI.—Percentage Dissociation.

v.	α 0°.	α 13°.5.	α 25°.	α 35°.
2	68.2	65.4	64.2	62.6
8	77.5	76.0	75.4	74.3
16	80.3	79.4	79.3	78.0
32	85.2	84.2	84.4	83.4
128	91.2	91.4	91.4	91.4
512	99.8	99.4	99.8	99.2
1024	100.0	100.0	100.0	100.0

Barium Chloride.

The sample of barium chloride was dried in an air-bath, for some hours, at 110°. The mother-solution was made up by direct weighing and the lesser concentrations obtained by dilution. The conductivity measurements were made at 5 different temperatures. In Table LXXIV., the calculated values of the molecular conductivities, at 18°, show a close agreement with those obtained, experimentally, by Kohlrausch and Krannhals, at the same temperature. In the case of dilute solutions, however, our values are somewhat lower.

Table LXXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 4°.6.	μ_v 16°.5.	μ_v 25°.	μ_v 35°.
2	86.62	96.61	128.2	150.0	178.6
8	99.06	112.3	151.1	179.0	215.3
16	105.2	119.5	161.2	191.6	230.4
64	116.2	132.4	180.2	215.2	260.3
256	125.1	142.7	194.7	232.9	282.6
512	126.5	144.3	197.2	235.5	286.2
1024	130.9	149.3	203.8	243.4	296.4
2048	132.7	151.2	206.3	247.1	300.5

Table LXXVIII.—Comparison with Work of Others.

	Kohlrausch.	Krannhals.	Calculated.
v.	μ_v 18°.	μ_v 18°.	μ_v 18°.
2	131.6	131.0	132.0
8	...	154.0	156.0
16	...	163.0	166.6
20	172.2	....	...
32	...	170.0	...
40	180.8	...	...
64	...	...	186.4
66.7	187.8	...	...
128	...	192.0	...
200	201.2	...	...
256	...	...	201.4
333	206.2	...	...
512	...	212.0	204.0
1000	214.8	...	...
1024	...	...	211.0
2000	218.4	224.0	...
2048	...	...	213.5

Table LXXIX.—Temperature Coefficients in Conductivity Units.

v.	0°–4°.6.	4°.6–16°.5.	16°.5–25°.	25°–35°.
2	2.17	2.66	2.56	2.86
8	2.88	3.26	3.28	3.63
16	3.11	3.50	3.58	3.88
64	3.52	4.02	4.12	4.51
256	3.83	4.36	4.49	4.97
512	3.87	4.45	4.51	5.07
1024	4.00	4.57	4.66	5.30
2048	4.02	4.63	4.80	5.34

Table LXXX.—Temperature Coefficients in Per Cent.

v.	0°–4°.6.	4°.6–16°.5.	16°.5–25°.	25°–35°.
2	2.51	2.75	2.00	1.91
8	2.91	2.90	2.17	2.02
16	2.96	2.93	2.22	2.03
64	3.03	3.04	2.29	2.10
256	3.06	3.06	2.30	2.13
512	3.06	3.08	2.29	2.19
1024	3.05	3.06	2.28	2.18
2048	3.03	3.06	2.33	2.16

Table LXXXI.—Percentage Dissociation.

v.	α 0°.	α 4°.6.	α 16°.5.	α 25°.	α 35°.
2	65.3	63.9	62.1	60.7	59.4
8	74.6	74.3	73.2	72.4	71.6
16	79.3	79.0	78.1	77.5	76.6
64	87.6	87.6	87.3	87.1	86.6
256	94.3	94.4	94.4	94.3	94.0
512	95.3	95.4	95.6	95.3	95.2
1024	98.6	98.7	98.8	98.5	98.6
2048	100.0	100.0	100.0	100.0	100.0

Magnesium Chloride.

The original solution was standardized gravimetrically, by determining the chlorine as silver chloride. As is shown by the tables, the effect of temperature on dissociation and on the temperature coefficient of conductivity, expressed in percentage of conductivity units, is of the same general nature as in the case of the other substances we have considered. In Tables LXXXII. and LXXXIII. the same temperature effect is likewise noticed.

Table LXXXII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 14°.9.	μ_v 25°.	μ_v 35°.
2	67.59	99.09	122.8	148.3
8	81.35	120.8	150.3	182.5
16	86.87	129.6	161.2	195.2
32	92.26	137.4	171.7	208.4
128	100.3	151.6	189.2	231.4
512	105.3	159.8	200.6	245.8
1024	106.9	162.5	203.2	249.1

Table LXXXIII.—Temperature Coefficients in Conductivity Units.

v.	0°-14°.9.	14°.9-25°.	25°-35°.
2	2.11	2.35	2.55
8	2.65	2.92	3.22
16	2.87	3.13	3.40
32	3.03	3.40	3.67
128	3.44	3.72	4.22
512	3.66	4.03	4.52
1024	3.73	4.03	4.59

Table LXXXIV.—Temperature Coefficients in Per Cent.

v.	0°-14°.9.	14°.9-25°.	25°-35°.
2	3.12	2.37	2.08
8	3.26	2.42	2.14
16	3.30	2.42	2.11
32	3.28	2.47	2.13
128	3.43	2.45	2.22
512	3.48	2.59	2.25
1024	3.49	2.48	2.26

Table LXXXV.—Percentage Dissociation.

v.	α 0°.	α 14°.9.	α 25°.	α 35°.
2	63.2	61.0	60.4	59.5
8	76.1	74.3	74.0	73.3
16	81.3	79.8	79.3	78.4
32	86.3	84.6	84.5	83.7
128	93.8	93.3	93.1	92.9
512	98.5	98.3	98.7	98.7
1024	100.0	100.0	100.0	100.0

Zinc Sulphate.

The specimen of salt used was dried for several days, in an air-bath, at 110°. This was found necessary to bring it to constant weight. It was preserved in a desiccator until required. In Table LXXXVII. the comparison of our values of the molecular conductivities, with the results obtained experimentally by Kohlrausch, at 18°, shows a very close agreement. Conductivity measurements, in the case of this salt, were made at only 3 temperatures.

Table LXXXVI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 15°.	μ_v 25°.
2	30.57	45.56	56.62
8	43.20	64.74	80.01
16	50.99	75.20	93.6
32	59.37	86.96	108.8
128	76.61	115.8	144.8
512	97.0	147.3	185.1
1024	104.7	156.9	197.8
2048	113.3	170.4	213.0
8192	117.0	176.0	218.0

Table LXXXVII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
2	49.8	48.89
4	60.4	. .
8	. .	69.33
16	. .	80.72
20	86.2	. .
1000	172.2	. .
1024	. .	169.14
2000	183.8	. .
2048	. .	183.3

Table LXXXVIII.—Temperature Coefficients in Conductivity Units.

v.	0°.15.	15°–25°.
2	0.999	1.11
8	1.44	1.53
16	1.61	1.84
32	1.84	2.18
128	2.61	2.90
512	3.36	3.78
1024	3.48	4.09
2048	3.80	4.26
8192	3.93	4.20

Table LXXXIX.—Temperature Coefficients in Per Cent.

v.	0°.15.	15°–25°.
2	3.27	2.44
8	3.33	2.36
16	3.16	2.45
32	3.10	2.51
128	3.41	2.50
512	3.46	2.57
1024	3.32	2.61
2048	3.35	2.50
8192	3.36	2.39

Table XC.—Percentage Dissociation.

v.	α 0°.	α 15°.	α 25°.
2	26.1	25.9	25.9
8	36.9	36.8	36.7
16	43.6	42.7	42.9
32	50.7	49.4	49.9
128	65.5	65.8	66.4
512	82.9	83.7	84.9
1024	89.5	89.2	90.7
2048	96.8	96.8	97.7
8192	100.0	100.0	100.0

Manganese Chloride.

The strength of the solution of this salt was determined avimetrically, the manganese being weighed as the oxide, n_3O_4.

Table XCI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.4.	μ_v 25°.	μ_v 35°.
2	68.14	89.64	121.3	145.0
8	84.98	113.5	156.7	188.1
16	91.79	121.9	169.0	205.1
32	97.4	130.0	181.6	221.2
128	107.0	143.8	202.5	246.7
512	114.1	154.0	216.6	264.5
1024	114.9	154.9	216.8	265.4

Table XCII.—Temperature Coefficients in Conductivity Units.

v.	0°-10°.4.	10°.4-25°.	25°-35°.
2	2.07	2.17	2.37
8	2.74	2.96	3.14
16	2.89	3.23	3.61
32	3.13	3.53	3.96
128	3.54	4.02	4.42
512	3.83	4.28	4.79
1024	3.85	4.24	4.86

Table XCIII.—Temperature Coefficients in Per Cent.

v.	0°-10°.4.	10°.4-25°.	25°-35°.
2	3.03	2.42	1.95
8	3.22	2.61	2.00
16	3.15	2.65	2.14
32	3.21	2.72	2.13
128	3.31	2.79	2.18
512	3.37	2.80	2.22
1024	3.35	2.74	2.24

Table XCIV.—Percentage Dissociation.

v.	α 0°.	α 10°.4.	α 25°.	α 35°.
2	59.3	57.9	56.0	54.6
8	74.0	73.3	72.3	70.9
16	79.0	78.7	78.0	77.3
32	84.8	83.9	83.8	83.1
128	93.1	92.8	93.4	93.0
512	99.3	99.4	99.9	99.7
1024	100.0	100.0	100.0	100.0

Manganese Nitrate.

The strength of the mother-solution was determined gravimetrically, the manganese being weighed as the oxide, Mn_3O_4.

Table XCV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 10°.2.	μ_v 25°.	μ_v 35°.
2	66.1	85.4	116.3	138.7
8	83.1	104.1	144.3	172.5
16	85.5	111.5	154.5	185.1
32	90.5	118.8	165.0	197.9
128	98.3	129.7	182.0	219.8
512	104.8	138.4	194.6	236.2
1024	105.4	139.3	195.8	237.4

Table XCVI.—Temperature Coefficients in Conductivity Units.

v.	0°-10°.2.	10°.2-25°.	25°-35°.
2	1.89	2.09	2.24
8	2.06	2.72	2.82
16	2.55	2.90	3.06
32	2.77	3.12	3.29
128	3.07	3.53	3.78
512	3.29	3.08	4.16
1024	3.33	3.82	4.16

Table XCVII.—Temperature Coefficients in Per Cent.

v.	0°-10°.2.	10°.2-25°.	25°-35°.
2	2.86	2.45	1.93
8	2.48	2.61	1.95
16	2.98	2.60	1.98
32	3.06	2.63	1.99
128	3.12	2.72	2.08
512	3.13	2.75	2.14
1024	3.15	2.74	2.13

Table XCVIII.—Percentage Dissociation.

v.	α 0°.	α 10°.2.	α 25°.	α 35°.
2	62.7	61.3	59.4	58.4
8	78.8	74.7	73.7	72.7
16	81.1	80.0	78.9	78.0
32	85.9	85.2	84.3	83.4
128	93.3	93.1	93.0	92.6
512	99.4	99.4	99.4	99.5
1024	100.0	100.0	100.0	100.0

Cobalt Chloride.

By means of several gravimetric determinations, as cobalt sulphate, the strength of the mother-solution was ascertained. From this the other solutions were obtained by dilution. It is apparent, from the tables, that results of the same character were obtained with cobalt chloride as with the other salts.

Hydrolysis probably came into play, to some extent, in the more dilute solutions.

Table XCIX.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 7°.2.	μ_v 25°.	μ_v 35°.
2	71.77	87.16	129.5	154.9
8	87.75	107.4	161.5	195.4
16	94.08	115.3	174.2	211.3
32	100.2	122.8	186.7	226.6
128	109.6	135.1	207.1	252.1
512	116.5	143.7	221.2	270.5
1024	116.8	144.0	221.1	270.6

Table C.—Temperature Coefficients in Conductivity Units.

v.	0°-7°.2.	7°.2-25°.	25°-35°.
2	2.14	2.38	2.54
8	2.73	3.04	3.39
16	2.95	3.31	3.71
32	3.14	3.59	3.99
128	3.54	4.04	4.50
512	3.77	4.35	4.93
1024	3.78	4.33	4.95

Table CI.—Temperature Coefficients in Per Cent.

v.	0°-7°.2.	7°.2-25°.	25°-35°.
2	2.98	2.73	1.96
8	3.11	2.83	2.10
16	3.14	2.87	2.13
32	3.13	2.92	2.14
128	3.23	2.99	2.17
512	3.23	3.03	2.22
1024	3.24	3.01	2.24

Table CII.—Percentage Dissociation.

v.	α 0°.	α 7°.2.	α 25°.	α 35°.
2	61.4	60.5	58.6	57.2
8	75.1	74.6	73.0	72.2
16	80.5	80.1	78.8	78.1
32	85.8	85.3	84.4	83.7
128	93.8	93.8	93.7	93.2
512	99.7	99.8	100.0	100.0
1024	100.0	100.0	100.0	100.0

Cobalt Nitrate.

The strength of the original solution was determined gravimetrically, the cobalt being weighed as sulphate.

The salt is probably hydrolyzed, to some extent, in very dilute solutions.

Table CIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 5°.4.	μ_v 25°.	μ_v 35°.
2	71.65	82.27	125.9	150.7
8	87.07	101.0	157.9	189.9
16	93.16	108.2	169.2	204.7
32	98.9	114.7	180.8	218.6
128	108.0	125.8	200.4	242.2
512	115.9	135.5	215.5	262.1
1024	116.1	135.4	215.3	262.0

Table CIV.—Temperature Coefficients in Conductivity Units.

v.	0°-5°.4.	5°.4-25°.	25°-35°.
2	1.97	2.23	2.48
8	2.39	2.90	3.20
16	2.79	3.11	3.55
32	2.92	3.37	3.78
128	3.30	3.81	4.18
512	3.63	4.08	4.66
1024	3.57	4.08	4.67

Table CV.—Temperature Coefficients in Per Cent.

v.	0°-5°.4.	5°.4-25°.	25°-35°.
2	2.75	2.71	1.97
8	2.74	2.87	2.03
16	2.99	2.87	2.09
32	2.95	2.94	2.09
128	3.06	3.03	2.09
512	3.13	3.01	2.16
1024	3.08	3.01	2.17

Table CVI.—Percentage Dissociation.

v.	α 0°.	α 5°.4.	α 25°.	α 35°.
2	61.7	60.8	58.5	57.5
8	75.0	74.6	73.3	72.5
16	80.2	79.9	78.6	78.1
32	85.2	84.7	84.0	83.4
128	93.0	92.9	93.1	92.4
512	99.8	100.0	100.0	100.0
1024	100.0	100.0	100.0	100.0

Nickel Chloride.

The original solution of nickel chloride was standardized electrolytically, according to the method of Smith and Exner. The salt was converted into sulphate, evaporated to dryness, the residue dissolved in ammonium sulphate and the solution treated with ammonia until strongly alkaline. The nickel was then determined electrolytically.

The salts of nickel, like those of cobalt, probably show small hydrolysis at high dilutions.

Table CVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 6°.3.	μ_v 25°.	μ_v 35°.
2	73.07	86.49	131.7	158.0
8	89.51	106.3	164.8	198.9
16	95.79	114.4	177.4	215.3
32	102.1	122.0	190.5	231.2
128	112.0	134.7	211.6	256.8
512	119.9	144.5	227.2	276.8
1024	120.7	145.4	229.0	279.4

Table CVIII.—Temperature Coefficients in Conductivity Units.

v.	0°-6°.3.	6°.3-25°.	25°-35°.
2	2.13	2.42	2.63
8	2.67	3.13	3.41
16	2.95	3.37	3.79
32	3.16	3.66	4.07
128	3.57	4.11	4.52
512	3.90	4.42	4.96
1024	3.92	4.47	5.04

Table CIX.—Temperature Coefficients in Per Cent.

v.	0°-6°.3.	6°.3-25°.	25°-35°.
2	2.91	2.80	2.00
8	2.98	2.94	2.07
16	3.08	2.95	2.14
32	3.10	3.00	2.14
128	3.19	3.05	2.14
512	3.25	3.06	2.18
1024	3.25	3.07	2.20

Table CX.—Percentage Dissociation.

v.	α 0°.	α 6°.3.	α 25°.	α 35°.
2	60.5	59.5	57.5	56.6
8	74.2	73.1	72.0	71.2
16	79.4	78.7	77.5	77.1
32	84.6	83.9	83.1	82.7
128	92.8	92.6	92.4	91.9
512	99.3	99.4	99.2	99.1
1024	100.0	100.0	100.0	100.0

Nickel Nitrate.

The standardization of the mother-solution of nickel nitrate was carried out in the same manner as in the case of nickel chloride. The nickel was determined electrolytically, according to the method of Smith and Exner.

Table CXI.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 6°.	μ_v 25°.	μ_v 35°.
2	71.34	83.06	125.3	150.4
8	87.35	102.7	157.9	190.0
16	93.67	109.9	169.7	204.8
32	99.15	116.8	180.9	218.6
128	108.3	128.7	200.1	242.9
512	116.1	137.2	215.4	261.3
1024	115.8	137.4	214.3	260.1

Table CXII.—Temperature Coefficients in Conductivity Units.

v.	0°-6°.	6°-25°.	25°-35°.
2	1.95	2.22	2.51
8	2.56	2.91	3.21
16	2.71	3.15	3.51
32	2.94	3.37	3.77
128	3.40	3.76	4.28
512	3.52	4.12	4.59
1024	3.60	4.05	4.58

Table CXIII.—Temperature Coefficients in Per Cent.

v.	0°-6°.	6°-25°.	25°-35°.
2	2.73	2.67	2.00
8	2.93	2.83	2.03
16	2.89	2.87	2.07
32	2.97	2.89	2.08
128	3.14	2.92	2.14
512	3.03	3.00	2.13
1024	3.11	2.95	2.14

Table CXIV.—Percentage Dissociation.

v.	α 0°.	α 6°.	α 25°.	α 35°.
2	61.6	60.5	58.5	57.8
8	75.4	74.7	73.7	73.0
16	80.9	80.0	79.2	78.7
32	85.6	85.0	84.4	84.0
128	93.5	93.7	93.4	93.4
512	100.0	99.9	100.0	100.0
1024	100.0	100.0	100.0	100.0

Copper Chloride.

The exact strength of the mother-solution was obtained by several gravimetric determinations. The copper was precipitated with sodium hydroxide and weighed as cupric oxide. The solution was then diluted to 0.5 N and from this the others were obtained by dilution.

Hydrolysis comes into play here to a greater extent than with any of the previous salts. This is shown in the conductivities, which continue to increase even at the highest dilutions studied. We think that the value of μ_v at 1000 liters is not widely removed from the true value of $\mu\infty$.

Table CXV.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 13°.8.	μ_v 25°.	μ_v 35°.
2	68.95	96.36	119.8	141.3
8	87.57	127.0	158.3	189.9
16	94.82	137.0	173.5	208.6
32	101.3	147.1	187.5	226.2
128	111.5	164.5	210.1	255.6
512	118.4	175.3	224.0	273.4
1024	123.0	181.7	232.2	282.6

Table CXVI.—Temperature Coefficients in Conductivity Units.

v.	0°-13°.8.	13°.8-25°.	25°-35°.
2	1.99	2.09	2.15
8	2.86	2.79	3.16
16	3.06	3.26	3.51
32	3.32	3.61	3.87
128	3.84	4.07	4.55
512	4.12	4.35	4.94
1024	4.25	4.51	5.04

Table CXVII.—Temperature Coefficients in Per Cent.

v.	0°-13°.8.	13°.8-25°.	25°-35°.
2	2.89	2.17	1.79
8	3.26	2.20	2.00
16	3.23	2.37	2.02
32	3.28	2.45	2.06
128	3.44	2.47	2.17
512	3.48	2.48	2.20
1024	3.46	2.48	2.17

Table CXVIII.—Percentage Dissociation.

v.	α 0°.	α 13°.8.	α 25°.	α 35°.
2	56.1	53.0	51.6	50.0
8	71.2	69.9	68.2	67.2
16	77.1	75.4	74.7	73.8
32	82.4	81.0	80.7	80.0
128	90.7	90.5	90.5	90.4
512	96.3	96.5	96.5	96.7
1024	100.0	100.0	100.0	100.0

Copper Nitrate.

The solution of this salt was standardized gravimetrically, the copper being weighed as cupric oxide. Conductivity measurements were made at 5 different temperatures. The effect of temperature on conductivity, temperature coefficients and dissociation is the same as with the other salts we have considered.

The remarks in reference to hydrolysis apply here, as in the case of copper chloride.

Table CXIX.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 5°.	μ_v 15°.8.	μ_v 25°.	μ_v 35°.
2	69.38	79.17	102.5	123.3	147.1
8	86.48	99.21	130.0	156.7	188.5
16	93.0	106.7	140.2	169.4	204.0
32	99.15	113.8	150.0	181.8	219.9
128	109.0	125.5	166.5	201.9	245.0
512	117.7	136.1	180.2	218.4	266.6
1024	119.8	138.6	183.3	222.9	271.7

Table CXX.—Temperature Coefficients in Conductivity Units.

v.	0°-5°.	5°-15°.8.	15°.8-25°.	25°-35°.
2	1.96	2.16	2.26	2.38
8	2.55	2.85	2.90	3.18
16	2.74	3.10	3.17	3.46
32	2.93	3.35	3.46	3.81
128	3.30	3.80	3.85	4.31
512	3.68	4.08	4.15	4.82
1024	3.76	4.14	4.30	4.88

Table CXXI.—Temperature Coefficients in Per Cent.

v.	0°-5°.	5°-15°.8.	15°.8-25°.	25°-35°.
2	2.83	2.73	2.20	1.93
8	2.95	2.87	2.23	2.03
16	2.95	2.91	2.26	2.04
32	2.95	2.94	2.31	2.10
128	3.03	3.03	2.33	2.14
512	3.13	3.00	2.30	2.21
1024	3.14	2.99	2.35	2.19

Table CXXII—Percentage Dissociation.

v.	α 0°.	α 5°.	α 15°.8.	α 25°.	α 35°.
2	57.9	57.1	55.9	55.3	54.1
8	72.2	71.6	70.9	70.3	69.4
16	77.6	77.0	76.5	76.0	75.1
32	82.8	82.1	81.9	81.6	80.9
128	91.0	90.5	90.8	90.6	90.2
512	98.2	98.2	98.3	98.0	98.0
1024	100.0	100.0	100.0	100.0	100.0

Hydrochloric Acid.

The original solution was prepared by dissolving pure hydrochloric acid in redistilled water. By means of the hydrometer the solution was diluted to approximately 0.25 N concentration. The exact strength was then determined by diluting the original solution five times and titrating successive portions by means of a standard solution of potassium hydroxide. The potassium hydroxide solution used had been carefully standardized against sulphuric acid, which, in turn, had been standardized gravimetrically by precipitation as barium sulphate. From the data thus obtained, the mother-solution was diluted with the proper volume of water to make it exactly 0.25 N. This dilution was then checked by titrating. The other solutions were obtained by diluting the original one.

Hydrochloric acid is a very strong acid. This is shown by the fact that a 0.25 N solution is dissociated more than 90 per cent and the value of $\mu\infty$ is obtained at a volume of about 128. Table CXXIV. shows a close agreement between the values of the molecular conductivities as found by Ostwald and Krannhals and those which we have obtained.

In Table CXXV., *the temperature coefficients in conductivity units decrease with rise in temperature.* This is true, in general, in the case of acids, while with salts the opposite is true. The effect of temperature on conductivity, percentage temperature coefficients of conductivity and dissociation is of the same general character as in the case of salts.

The temperature coefficients, in conductivity units, are very high and also the conductivities. This is due to the acid being one of the very strongest and the hydrogen ion being the swiftest of all ions.

Table CXXIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 25°.
4	223.3	285.9	348.2	397.9
8	227.0	292.2	357.0	407.1
16	231.8	298.7	365.2	415.5
32	235.0	303.3	370.7	423.4
128	238.8	309.0	379.3	433.3
512	235.5	304.2	374.7	428.3
1024	221.5	287.7	353.4	405.3

Table CXXIV.—Comparison with the Work of Others.

	Ostwald.	Krannhals.	Calculated.
v.	μ_v 25°.	μ_v 18°.	μ_v 18°.
4	343	313	313.3
8	355	323	320.7
16	362	329	328.0
32	369	335	333.0
128	376	341	340.0

Table CXXV.—Temperature Coefficients in Conductivity Units.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	5.01	4.98	4.97
8	5.22	5.18	5.01
16	5.35	5.32	5.03
32	5.46	5.39	5.27
128	5.62	5.62	5.40
512	5.50	5.64	5.36
1024	5.30	5.26	5.19

Table CXXVI.—Temperature Coefficients in Per Cent.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	2.24	1.74	1.43
8	2.30	1.77	1.40
16	2.31	1.78	1.38
32	2.37	1.77	1.42
128	2.35	1.82	1.42
512	2.34	1.85	1.43
1024	2.39	1.83	1.47

Table CXXVII.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
4	93.5	92.5	91.8	91.8
8	95.1	94.6	94.1	93.9
16	97.1	96.7	96.3	95.9
32	98.4	98.2	97.7	97.7
128	100.0	100.0	100.0	100.0

Nitric Acid.

The solution was prepared and standardized in the same manner as that of hydrochloric acid.

Results of the same general character were obtained with nitric acid as with hydrochloric acid. In Table CXXIX., the temperature coefficients, expressed in conductivity units, decrease with rise in temperature. Like hydrochloric acid, nitric acid is also a very strong electrolyte. The value of $\mu\infty$ is obtained at a value of about 128.

The same remarks apply to the temperature coefficients and the conductivity of nitric as to those of hydrochloric acid.

Table CXXVIII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 12°.5.	μ_v 25°.	μ_v 35°.
4	222.4	284.3	344.4	390.8
8	226.9	290.5	354.4	402.7
16	231.3	296.3	362.0	411.8
32	235.4	301.7	368.7	418.6
128	238.3	308.2	376.6	429.4
512	236.7	306.0	373.9	426.9
1024	231.4	299.9	366.5	419.8

Table CXXIX.—Temperature Coefficients in Conductivity Units.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	4.95	4.81	4.64
8	5.09	5.11	4.83
16	5.20	5.25	4.98
32	5.30	5.36	4.99
128	5.59	5.47	5.28
512	5.54	5.43	5.30
1024	5.48	5.33	5.33

Table CXXX.—Temperature Coefficients in Per Cent.

v.	0°-12°.5.	12°.5-25°.	25°-35°.
4	2.23	1.69	1.35
8	2.24	1.76	1.36
16	2.25	1.77	1.38
32	2.25	1.78	1.35
128	2.34	1.77	1.40
512	2.34	1.77	1.42
1024	2.37	1.78	1.45

Table CXXXI.—Percentage Dissociation.

v.	α 0°.	α 12°.5.	α 25°.	α 35°.
4	93.3	92.2	91.4	91.0
8	95.2	94.3	94.1	93.8
16	97.1	96.1	96.1	95.9
32	98.8	97.9	97.6	97.5
128	100.0	100.0	100.0	100.0

Sulphuric Acid.

By means of the hydrometer and Lunge's tables, a solution approximately 0.25 N was made. A portion of this was then diluted ten times and this diluted portion standardized by precipitation with barium chloride. From the data thus obtained, the mother-solution was diluted to exactly 0.25 N. This dilution was then checked by further precipitation. The comparisons, given in Table CXXXIII., between our calculated results and those obtained experimentally by Kohlrausch at 18°, are not quite as satisfactory as the comparisons with other substances.

Table CXXXII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 16°.3.	μ_v 25°.	μ_v 35°.
4	292.9	382.8	419.3	457.2
8	303.9	393.9	431.5	471.7
16	323.6	417.3	456.6	498.0
32	347.2	450.0	491.4	533.6
128	403.6	535.6	589.4	646.2
512	442.7	601.1	675.2	753.0
2048	449.2	622.4	709.9	814.4
8192	441.6	618.2	708.6	816.3

Table CXXXIII.—Comparison with the Work of Kohlrausch.

	Kohlrausch.	Calculated.
v.	μ_v 18°.	μ_v 18°.
4	379.8	389.9
16	...	425.0
20	416.8	...
32	...	458.1
40	468.6	...
128	...	546.1
200	571.0	...
333	600.2	...
512	...	615.6
2000	663.2	...
2048	...	639.5

Table CXXXIV.—Temperature Coefficients in Conductivity Units.

v.	0°-16°.3.	16°.3-25°.	25°-35°.
4	5.52	4.20	3.79
8	5.52	4.32	4.02
16	5.75	4.52	4.14
32	6.31	4.76	4.22
128	8.10	6.18	5.68
512	9.72	8.52	7.78
2048	10.63	10.06	10.45
8192	10.83	10.39	10.77

Table CXXXV.—Temperature Coefficients in Per Cent.

v.	0°-16°.3.	16°.3-25°.	25°-35°.
4	1.88	1.10	0.90
8	1.49	1.10	0.93
16	1.78	1.08	0.91
32	1.82	1.06	0.86
128	2.01	1.15	0.96
512	2.19	1.42	1.15
2048	2.37	1.62	1.47
8192	2.45	1.68	1.52

Table CXXXVI.—Percentage Dissociation.

v.	α 0°.	α 16°.3.	α 25°.	α 35°.
4	65.2	61.5	59.1	56.1
8	67.7	63.3	60.8	57.9
16	72.0	67.0	64.3	61.2
32	77.3	72.3	69.2	65.5
128	89.8	86.1	83.0	79.3
512	98.6	96.6	95.1	92.5
2048	100.0	100.0	100.0	100.0

Oxalic Acid.

The sample of oxalic acid used was purified by repeated crystallizations and was then thoroughly air-dried. The mother-solution was made up by direct weighing, the others being obtained by dilution. As is shown by the values of the molecular conductivities given in Table CXXXVII., oxalic acid is much weaker than the other acids we have considered. With it, as with other acids and salts which we have studied, the effect of rise in temperature from 0° to 35° is to decrease the percentage temperature coefficients of conductivity.

Table CXXXVII.—Molecular Conductivities.

v.	μ_v 0°.	μ_v 11°.8.	μ_v 25°.	μ_v 35°.
2	79.43	100.1	123.1	135.6
8	123.5	156.3	189.8	212.3
16	147.2	186.4	227.1	255.2
32	169.8	215.1	262.3	295.8
128	203.8	260.2	318.9	361.1
512	223.7	285.3	349.9	397.1
2048	240.2	307.4	375.6	428.1
8192	265.0	334.0	412.0	466.0

Table CXXXVIII.—Temperature Coefficients in Conductivity Units.

v.	0°-11°.8.	11°.8-25°.	25°-35°.
2	1.75	1.74	1.25
8	2.77	2.54	2.25
16	3.32	3.08	2.81
32	3.84	3.58	3.35
128	4.78	4.45	4.22
512	5.22	4.89	4.72
2048	5.69	5.17	5.25
8192	5.85	5.91	5.40

Table CXXXIX.—Temperature Coefficients in Per Cent.

v.	0°-11°.8.	11°.8-25°.	25°-35°.
2	2.20	1.74	1.02
8	2.24	1.63	1.19
16	2.26	1.65	1.24
32	2.26	1.67	1.28
128	2.35	1.71	1.32
512	2.33	1.71	1.35
2048	2.36	1.68	1.40
8192	2.21	1.77	1.31

Discussion of Results.

It was pointed out in the historical review of this subject, that up to the present no final conclusions had been reached as to the exact effect of temperature on dissociation, over the range of temperature from 0° to 35°. A number of investigators have made conductivity measurements at different temperatures, but concordant results have not been obtained by those who have worked in this field. Moreover, no one has studied the exact temperature effect for any very large number of substances having different degrees of dissociation.

We have studied, in all, 32 substances, inorganic and organic, with very different degrees of dissociation. Without a single exception, results of the same character have been obtained with every one of them. The percentage dissociation and the percentage temperature coefficients of conductivity decrease with rise in temperature. The effect of temperature on the temperature coefficients of conductivity, expressed in conductivity units, is, however, different in the case of salts from that in the case of acids. This fact has been clearly demonstrated. With salts, the temperature coefficients of conductivity, expressed in conductivity units, increase with rise in temperature, while, in the case of acids, they decrease with rise in temperature.

A number of tables have been incorporated, showing a comparison of our results with those of others. As we have seen, the agreement between the two sets of values has been, in general, satisfactory.

Sufficient evidence has, undoubtedly, been obtained in this investigation to justify the conclusion that the percentage dissociation and the percentage temperature coefficients of conductivity decrease with rise in temperature, from 0° to 35°.

From the data presented, it is apparent that the tables representing the percentage temperature coefficients of conductivity and percentage dissociation run parallel. The percentage temperature coefficients of conductivity and the percentage dissociation decrease with rise in temperature. These facts are interesting in the light of certain hypotheses, which have been advanced in recent years.

Dutoit and Aston[1] have suggested the following relation; that only in those solvents which are polymerized or associated, do dissolved substances conduct the current. That is, the more associated a solvent the greater its dissociating power. Dutoit and Friderich[2] have also shown this relation to be true in a number of cases.

Ramsay and Shields[3] proved that in many liquids the molecules are not the simplest possible, but are aggregates of these simplest molecules, having various degrees of complexity; that is, the liquid molecules are polymerized aggregates of the simplest molecules. Water, one of the strongest dissociants, has a high degree of association. At 0° the molecule is $(H_2O)_4$. As the temperature is raised, the association becomes less, as Ramsay and Shields showed by the following data:

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[1] Compt. rend., **125**, 540 (1897).

[2] Bull. Soc. Chim., [3], **19**, 321 (1898).

[3] J. Chem. Soc., **63**, 1089 (1893).

	0°.	10°.	20°.	30°.	40°.
Association factor x	4	3.81	3.68	3.44	3.18

It is obvious that, as the temperature of an aqueous solution of an electrolyte is increased, the ionic mobility is increased. At the same time the solvent water is becoming less and less associated with rise in temperature. As the association of the solvent decreases its dissociating power becomes less, according to the hypothesis of Dutoit and Aston. Thus we have two conditions affecting conductivity with rise in temperature, and they work counter to each other. The ions move faster with rise in temperature, increasing the conductivity. The association of the solvent becomes less with rise in temperature and, consequently, its dissociating power becomes less. This diminishes the conductivity. These facts are brought out very clearly by the data presented.

We have seen that conductivity increases with rise in temperature, the percentage of increase in conductivity per degree, decreases with rise in temperature, and the dissociation decreases with rise in temperature. In brief, when the temperature of an aqueous solution of an electrolyte is raised, the association of the water is decreased. The effect of this is to diminish its dissociating power and this, in turn, decreases the dissociation of the dissolved substance. Dissociation, then, is driven back by rise in temperature. The conductivity of a solution is conditioned by the number of ions present and by their velocity. The effect of decrease in dissociation with rise in temperature is to reduce the amount of conducting substance, or the number of ions in the solution. Consequently, although conductivity increases with rise in temperature, due to increase in ionic mobility, the percentage of increase in conductivity, per degree, should decrease ; otherwise, the conductivity-temperature curve would not reach a maximum with rise in temperature. This fact is clearly brought out and is in harmony with previous work at high temperatures, which shows a maximum in the conductivity curve with rise in temperature. It is also in harmony with the idea advanced by Bousfield and Lowry, in their curve representing the effect of temperature on the conductivity of a composite electrolyte. The curve reaches a maximum and then drops.

The results presented in these tables are interesting in connection with the hypothesis of Thompson and Nernst. J. J. Thompson[1] and, a little later, Nernst[2] pointed out that, if the forces which hold the atoms in the molecule are of an electrical nature, those solvents that have the highest dielectric constants should have the greatest dissociating power.

The work which has, thus far, been done shows that this is, in general, true.[3] O. U. Vonwiller[4] studied the dielectric constant of water, at various temperatures ranging from 0° to 28° and found that, with rise in temperature, the dielectric constant of water gradually decreased. If the dielectric constant of a solvent decreases with rise in temperature, then, according to the hypothesis of Thompson and Nernst, its dissociating power should decrease with rise in temperature. Consequently, the dissociation of the dissolved substance should decrease as the temperature rises. Fact and theory are in accord. We have shown that there is a decrease in dissociation with rise in temperature. The work of Vonwiller is, then, a connecting link between the Thompson-Nernst hypothesis and the experimental results obtained in this investigation. A number of electrolytes have been examined and, in each case, results of the same general character have been obtained.

It thus seems to be proved experimentally, for a large number of substances, what a few investigators have made probable for a few substances, over a wide range of temperature. Our results are in harmony with previous work at high temperatures, showing a maximum in the conductivity-temperature curve with rise in temperature, and also with the hypothesis of Bousfield and Lowry, in their curve representing the effect of temperature on the conductivity of a composite electrolyte. That there is a satisfactory agreement between the results of our experiments, the hypothesis of Dutoit and Aston and the work of Ramsay and Shields has been clearly demonstrated. We have also referred to the results of Vonwiller, and pointed out the fact that the Thompson-Nernst hypothesis holds admirably, in aqueous solutions, over a considerable range of temperature. When the temperature of an aqueous solution of an electrolyte is increased from 0° to 35°, the results expressed in tabular form are as follows:

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[1] Phil. Mag., **36**, 320 (1894).

[2] Z. physik. Chem., **13**, 531 (1894).

[3] Jones and Carroll : THIS JOURNAL, **32**, 521 (1904).

[4] Phil. Mag., [6], **7**, 655 (1904).

With rise in temperature from 0° to 35°.

Association of solvent decreases.
Dielectric constant of solvent decreases.
Viscosity of solvent decreases.
Dissociation of dissolved substance decreases.
Percentage temperature coefficients of conductivity decrease.
Ionic mobility increases.

SUMMARY AND CONCLUSIONS.

When the temperature of an aqueous solution of an electrolyte is raised from 0° to 35°, the effect of rise in temperature on conductivity, dissociation and on the temperature coefficient of conductivity has been determined and the following relation shown to exist:

Effect of Rise in Temperature from 0° to 35°.

1. A large increase in conductivity, due to increase in ionic mobility.

2. A small decrease in dissociation, in accordance with the law of Dutoit and Aston, connecting association of solvent and dissociation of dissolved substance, and in accordance with the results of Ramsay and Shields, showing a decrease in the association of water with rise in temperature.

3. From the results of Vonwiller, showing a decrease in the dielectric constant of water with rise in temperature, and the Thompson-Nernst hypothesis, connecting the dissociating power of a solvent with its dielectric constant, we should expect a decrease in dissociation with rise in temperature. This

has been demonstrated experimentally over a considerable range of temperature.

4. The temperature coefficients of conductivity, expressed in percentage of conductivity units, decrease with rise in temperature, and this fact is in accordance with the maximum in the conductivity-temperature curve of an electrolyte, as pointed out by Bousfield and Lowry, and with the work of former investigators at high temperatures.

5. The temperature coefficients of conductivity, expressed in conductivity units, in the case of salts increase with rise in temperature, while with acids they decrease with rise in temperature.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1905.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF TETRABROMORTHOBENZOQUINONE.[1]

BY C. LORING JACKSON AND H. A. CARLTON.

In this paper we describe the continuation of the work on the action of alcohols on tetrabromorthobenzoquinone, $C_6Br_4O_2$, begun some years ago by Porter and one of us.[2]

When methyl alcohol is allowed to stand, at ordinary temperatures, with tetrabromorthoquinone, a red compound[2] is formed at first, which is later converted into the α-addition-compound, $(C_6Br_4O_2)_2.CH_3OH$. The nature of this red compound could not be established by analysis, because the differences in percentage composition between the most probable formulas fell well within the limits of experimental accuracy, we accordingly resorted to a series of synthetic experiments, which showed that it was formed by the union of 2 molecules of tetrabromorthoquinone with 1 of the α-body, its formula, therefore, is $(C_6Br_4O_2)_4.CH_3OH$, and it may be called the methyl alcohol tetrakis tetrabromorthobenzoquinone. We could not obtain a corresponding compound with benzyl alcohol, but from the phenomena observed in the action of ethyl alcohol on tetrabromorthoquinone we think it probable one is formed in that case.

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by H. A. Carlton.

[2] THIS JOURNAL, 31, 89 (1904).

When the red methyl alcohol compound, $(C_6Br_4O_2)_4.CH_3OH$, was warmed with a dilute solution of sodic hydrate, it was converted into the β-methyl alcohol compound, $(C_6Br_4O_2)_2.CH_3OH$. This observation led us to try the action of sodic hydrate on the α-bodies and we found that this reagent converted the methyl and benzyl compounds into the corresponding β-compounds, thus furnishing a good general method for making the β-compounds, which was much needed, as the only one known before (action of acetic anhydride) gave very impure products.

Experiments with ethyl alcohol, normal propyl alcohol and isoamyl alcohol resulted in the preparation of new α- and β-compounds. Tertiary butyl alcohol also seemed to give an α-compound, but our supply of the alcohol was not large enough to obtain it pure. In the following table the decomposition or melting-points of all the known bodies of these two classes are recorded. We have nothing to add to the statement of their general properties already given :[1]

	α.	β.
$(C_6Br_4O_2)_2.H_2O$	190°–200°	221°–222°
$(C_6Br_4O_2)_2.CH_3OH$	178°–182°	261°
$(C_6Br_4O_2)_2.C_2H_5OH$	180°–185°	228°
$(C_6Br_4O_2)_2.C_3H_7OHn$	180°	176°
$(C_6Br_4O_2)_2.C_5H_{11}OHi$	150°	177°
$(C_6Br_4O_2)_2.C_7H_7OH$	165°–170°	216°–217°

The α-isoamyl compound melts without reddening, but at a higher temperature (190°) it is converted into the red hexabromorthoquinopyrocatechin ether like the other α-bodies.

We have spent much time on the reduction of the α-bodies, as we hoped that this work might settle their constitution, but we found that the same product was formed from the water, methyl alcohol, or benzyl alcohol compounds, showing that the alcohol (or water) was split off and there also seemed to be a deeper decomposition of the molecule, the fragments of which recombined to form the final product. We assign to this compound, melting at 274°–275°, the formula[1] $C_{18}Br_8O_6H_4$, which agrees with our analyses and with the discovery of a triacet derivative, melting at 273°–275° and a tribenzoyl derivative, melting at 250°–255°. Some unfinished experiments on the oxidation of the reduced substance showed that nitric acid converted it into a red product with essentially the same percentage of bromine, but treatment with chloroform separated this product into red prisms, melting at about 275°–280° and yellow needles not melting at 310°. The work must be repeated on a much larger scale to obtain enough of these bodies to determine their nature.

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[1] THIS JOURNAL, 31, 90 (1904).

The formula $C_{18}Br_8O_6H_4$ can be developed into

$$C_6Br_4 : O_2 : C_6H(OH)_2\, O.C_6Br_4OH,$$

which explains all the observed facts, but much more experimental work is necessary before it can be considered established. For purposes of indexing it may be called, provisionally, *octobromdihydroxyhemipyrocatechinepyrocatechine ether.* Such a substance would be formed from compounds with either of the two formulas[2] assigned to the α-bodies by reactions which involve no very strained hypotheses, and are about equally probable, so that these experiments throw no light on the structure of the α-compounds.

Some experiments with the β-compounds established little beyond confirming the previous observation that they are very stable substances.

EXPERIMENTAL.

The tetrabromorthobenzoquinone used by us was prepared by the method of Zincke,[3] with the modifications described in other papers[4] from this laboratory. We have found, however, if the quinone, after its formation, is precipitated by the addition of 1200 cc. of water instead of 300 cc., that the yield is larger and there is no diminution in the purity of the product. The preparations used by us melted generally between 145°–147°, in some cases as high as 150°, instead of 150°–151°, but the loss in purification is so great that we did not attempt to recrystallize them and, as a matter of fact, such specimens proved to be quite pure enough for our work.

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[1] The percentage of bromine in this substance, 67.05, is so close to that in $(C_6Br_4O_2)_2H_4.C_7H_7OH$ (66.67) that Porter and one of us (THIS JOURNAL, **31**, 105) assigned to it this incorrect formula.

[2] THIS JOURNAL, **31**, 93 (1904).

[3] Ber. d. chem. Ges., **20**, 177 (1887).

[4] Jackson and Koch: THIS JOURNAL, **26**, 34 (1901). Jackson and Porter: *Ibid.*, **30**, 522 (1903).

Red Compound of Tetrabromorthoquinone and Methyl Alcohol.

This substance was obtained by Porter and one of us[1] as the first product of the action of cold methyl alcohol on the orthoquinone, since it is usually formed after standing for 24 hours, but in that paper only analyses of the substance are given, which are not enough to establish its composition, as the differences between the percentages of the elements in the most probable formulas are nearly, if not quite, within the limits of experimental error. In taking up the subject again we tried to settle the composition of the substance by the following synthetic experiments:

In the first place it was found that the red compound could be formed by the action of tetrabromorthoquinone on the α-compound of tetrabromorthoquinone and methyl alcohol,[2] $(C_6Br_4O_2)_2.CH_3OH$ (formed by longer action of methyl alcohol on the quinone). Accordingly:

(1) Five tenths gram of the α-body were mixed with 0.24 gram of tetrabromorthoquinone dissolved in 5 cc. of benzene, giving the proportion of 1 molecule of the quinone to each molecule of the α-body. The greater part of the α-body remained undissolved in the bottom of the flask, but after standing over night it was found that small, dark-red prisms had begun to crystallize out of the benzene and that the white α-compound was partially converted into a red substance. After 24 hours the reaction seemed to be complete, as no more of the white substance was converted into the red, but for greater certainty the mixture was allowed to stand for 2 more

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[1] THIS JOURNAL, 31, 96 (1904).

[2] *Ibid.*, 31, 97 (1904).

days. The benzene was then poured off, mixed with a little ligroin and allowed to evaporate spontaneously. In this way small, dark-red crystals were obtained, which were recognized by their melting-point, 194°–195°, and crystalline form as the red methyl alcohol compound. The residue in the flask consisted of the red substance and the α-body, showing that more than 1 molecule of the quinone was needed to convert the α-compound into the red body.

(2) Five-tenths gram of the α-body were mixed with a solution of 0.48 gram tetrabromorthoquinone in 5 cc. of benzene, that is, 2 molecules of the quinone for each molecule of the α-body. The experiment ran as in (1) except that all the α-compound was converted into the red crystals melting at 194°–195° and the benzene solution, when allowed to evaporate with a little ligroin, gave only these crystals with a small amount of a red tar around the edges, no α-body or quinone being visible.

(3) Five-tenths gram of the α-body were mixed with 0.72 gram of tetrabromorthoquinone, that is, 3 molecules of the quinone to each molecule of the other component. The reaction in this experiment ran much more rapidly than in the other two, as the red compound began to crystallize out in half an hour. Finally all the white α-body was converted into the red product and the benzene, when mixed with ligroin and allowed to evaporate, yielded a mixture of the red prisms of the methyl alcohol body and the long red needles of tetrabromorthoquinone.

It is evident, from these experiments, that the red compound is formed by the union of 2 molecules of tetrabromorthoquinone with 1 of the α-body, $(C_6Br_4O_2)_2.CH_3OH$. This result is in harmony with the analyses, as shown by the following table, in which the results obtained by Porter[1] and an analysis of the product of Experiment 2 are compared with those calculated for the formula established by the syntheses.

0.1885 gram substance gave, by the Carius method, 0.3280 gram AgBr.

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[1] This Journal, 31, 96 (1904).

	Calculated for $(C_6Br_4O_2)_4.CH_3OH$.	Found. Porter.		Found. Carlton.
C	17.36	17.48		. .
H	0.23	0.66		. .
Br	74.08	73.83	73.90	74.03

Properties of the Red Compound, Methylalcoholtetrakistetrabromorthobenzoquinone.—As observed by Porter, it crystallizes in small, transparent, well-formed prisms of a cherry-red color, which are soluble in alcohol or benzene. Benzene mixed with ligroin is the best solvent for it. It usually crystallizes unaltered from this mixture, but occasionally it is decomposed partially under these conditions, yielding the α-body and tetrabromorthoquinone. Our observations on its behavior toward heat differ slightly from those of Porter, as we found it melts at 194°–195° instead of at 192°–193, and it is not stable at temperatures below its melting-point, as he states, but, if heated slowly, decomposes somewhat above 140°, forming a brick-red substance. Under these circumstances the difference of 2° between the earlier and later determinations of the melting-point is not surprising ; in fact, the melting-point 194°–195° could be obtained only by dipping the tube into the hot bath, so as to make the heating as short as possible. When the red compound is allowed to stand in the cold with methyl alcohol, it gradually turns white and at the end of 2 weeks is completely converted into the α-compound of tetrabromorthoquinone and methyl alcohol. A dilute solution of sodic hydrate converts the red substance into a white body, as described later in this paper.

An attempt to prepare a substance similar to the red methyl compound just described from the α-benzyl alcohol tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_7H_7OH$, gave a negative result. This α-body was mixed with a benzene solution of the quinone in the proportion of 2 molecules of the latter to each molecule of the former, but after standing a week the white α-benzyl compound remained unchanged on the bottom of the flask.

Action of Sodic Hydrate on the Red Methyl Alcohol Compound.

When the methyl alcohol tetrakistetrabromorthoquinone,

$(C_6Br_4O_2)_4.CH_3OH$,

was treated with a dilute solution of sodic hydrate, it was gradually converted into a white product and the alkaline solution assumed a dark, brownish-yellow color. After heating on the water-bath for an hour the liquid was poured off and was found to give a test for bromine with chlorine water and chloroform. The white solid product was washed three times with hot water by decantation, when it was found to turn dark at 200° and melt at 245°. On crystallization from benzene white crystals were obtained, which melted at 259°–260° and agreed in their other properties with the β-methyl alcohol compound, $(C_6Br_4O_2)_2.CH_3OH$. The red compound, therefore, is converted into the β-compound by hot sodic hydrate, in aqueous solution.

Action of Sodic Hydrate on Orthoquinone Addition Compounds of the Alpha Series.

As the work described in the preceding paragraph showed that sodic hydrate converted the red methyl compound into the β-methyl compound, it occurred to us that it might have a similar effect on the α-compounds, and the following experiments show that this is the case; we have, therefore, in the action of sodic hydrate, a good general method for converting α- into β-compounds, which was much needed.

Sodic Hydrate and the α-Benzyl Alcohol Compound.—One gram of the α-compound, $(C_6Br_4O_2)_2.C_7H_7OH$, was heated on the steam-bath with dilute sodic hydrate, for 1 hour. At the end of this time the orange-red solution was poured off from the white, insoluble portion. This liquid smelled of benzyl alcohol, but gave no test for bromine with chlorine water and chloroform. The solid was washed three times by decantation with hot water and melted, in this crude state, at 200°–210°, but recrystallization from a mixture of benzene and ligroin soon raised it to the constant melting-point 218°–219°. The melting-point of the β-benzyl alcohol compound was determined by Porter and one of us[1] as 216°–217°, but as our product shows all the properties of the β-compound, we ascribe this difference in the melting-point to the greater purity of our preparation, since the acetic anhydride method of making the β-compound—the only one known to Porter—gives a very impure product, which it is hard to purify thoroughly. For greater safety our product was dried at 100° and analyzed with the following result:

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[1] This Journal, 31, 104 (1904).

0.1659 gram substance gave 0.2613 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_7H_7OH$.	Found.
Br	66.95	67.01

Sodic Hydrate and the α-Methyl Alcohol Compound.—The α-methyl alcohol compound, $(C_6Br_4O_2)_2.CH_3OH$, after it had been heated with dilute sodic hydrate, on the steam-bath, for an hour, was converted into a pure white substance which, after recrystallization from benzene, showed the constant melting-point 259°–261° and was also identified with the β-compound by its other properties.[1]

Action of Other Alcohols on Tetrabromorthobenzoquinone.

The object of this work was to determine whether other alcohols formed α- and β-compounds with tetrabromorthoquinone similar to those obtained with methyl alcohol and with benzyl alcohol.

α-Compound from Ethyl Alcohol, $(C_6Br_4O_2)_2.C_2H_5OH$.—Five grams of tetrabromorthoquinone were mixed thoroughly with 10 cc. of absolute alcohol and the mixture allowed to stand in a corked flask, at ordinary temperatures. After 1 day there appeared a mass of orange crystals mixed with a few that were white. At the end of a week the liquid had become green and the white substance had disappeared entirely, but after 2 weeks there was a new deposit of white crystals. The mixture was allowed to stand 1 week more (4 weeks in all) to secure the completion of the reaction, and the crystals were then filtered out, washed with alcohol, recrystallized from a mixture of 1 part of benzene with 2 of alcohol and then dried at 100° for analysis.

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[1] The formation of the β-compounds, by the action of sodic hydrate, explains the behavior of the α-benzyl alcohol compound with sodium amalgam. THIS JOURNAL, 31, 106.

0.1639 gram substance gave, by the Carius method, 0.2772 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_2H_5OH$.	Found.
Br	71.60	71.96

That the substance belongs to the α-series is shown by its behavior when heated; at 150° it begins to redden and at 180°–185° melts to a bright red liquid, which is soon converted into a red solid. As this is a decomposition-point rather than a melting-point, a more definite temperature cannot be given.

Properties of the α-Ethyl Alcohol Tetrabromorthoquinone.—It crystallizes from benzene and alcohol in small, white, spherical bodies made up of very minute crystals. Its behavior with heat is described in the preceding paragraph. It is freely soluble in benzene, ether, chloroform, acetone, or carbonic disulphide; nearly insoluble in cold alcohol, but fairly soluble in it when hot; insoluble in cold ligroin or glacial acetic acid, slightly soluble in hot; essentially insoluble in water; unaffected by the three strong acids.

β-Ethyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_2H_5OH$.—This compound could not be obtained from the α-body by boiling it with alcohol. In fact, so far as our experience goes, that method of converting an α- into a β-body applies only to the methyl compound. Accordingly, we obtained the β-compound by the sodic hydrate method described earlier in this paper. Two grams of the crude α-compound, made as just described, were heated on the steam-bath, for an hour, with a dilute solution of sodic hydrate. The resulting reddish-brown liquid was poured off and the white solid, after washing three times with hot water, was recrystallized from a mixture of 1 part of benzene with 2 of alcohol, until it showed the constant melting-point 228°, when it was dried at 100° and analyzed.

0.1672 gram substance gave 0.2819 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_2H_5OH$.	Found.
Br	71.60	71.74

Properties of the β-Ethyl Alcohol Tetrabromorthoquinone.—It crystallizes in small, white, rhombic plates and melts at 228° without darkening or other signs of decomposition. It is freely soluble in benzene, ether, chloroform, acetone, or carbonic disulphide; essentially insoluble in cold glacial acetic acid, soluble in it when hot; essentially insoluble in cold alcohol or ligroin, slightly soluble when hot; insoluble in water. It is not affected by the three strong acids whether cold or hot.

α-Normal Propyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_3H_7OH$.—Five grams of the tetrabromorthoquinone were thoroughly mixed with 10 cc. of normal propyl alcohol and the mixture was allowed to stand, at ordinary temperatures, in a corked flask. After a few days small orange prisms appeared, and after 2 weeks the action seemed to be complete, but it was allowed to stand 2 weeks longer to make sure. The solid product consisted of orange prisms mixed with a few red crystals. It was washed with a mixture of 1 part of benzene with 2 of ligroin and then recrystallized from a mixture of equal parts of these two solvents, after which it was dried at 100° and analyzed.

0.1539 gram substance gave 0.2554 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_3H_7OH$.	Found.
Br	70.46	70.62

As it decomposed with reddening when heated, it belongs to the α-series. It crystallized in small, transparent prisms of a light-yellow color and resembles the α-ethyl body in its other properties. It begins to turn red at 150° and melts to a red liquid at 180°.

β-Normal Propyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_3H_7OH$.—One and one-half grams of the α-compound were heated on the steam-bath, for 1 hour, with a dilute solution of sodic hydrate. The yellow, alkaline liquid was then poured off and the solid product purified in the same way as the ethyl compound. It melted constantly at 176° and was dried at 100° for analysis:

0.1535 gram substance gave 0.2546 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_3H_7OH$.	Found.
Br	70.46	70.57

It crystallizes in small, white, six-sided plates and melts at 176° to a light-yellow liquid. In its other properties it resembles the β-ethyl compound.

α-Isoamyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_5H_{11}OH$.—Five grams of tetrabromorthoquinone were thoroughly mixed with 10 cc. of isoamyl alcohol and allowed to stand at ordinary temperatures, in a corked flask. After 1 day, long orange crystals appeared and after 2 weeks the quinone was, apparently, entirely converted into this substance, but it was allowed to stand another week to make sure that the reaction was complete. The product, consisting of orange prisms mixed with a small amount of a red substance, was filtered out, washed with a mixture of benzene and ligroin and crystallized from ligroin. In this way two sorts of crystals were obtained, transparent yellow prisms and opaque rosettes of a pale-yellow color. These prisms melted at 150° to a yellow liquid, which gradually turned red and solidified at about 190°. The rosettes melted at 105° to a yellow liquid, also turning red and solidifying at about 190°. The rosettes, which formed the larger part of the product, were separated mechanically and recrystallized from ligroin, the resulting crystals were almost entirely prisms melting at 150°, while the few rosettes obtained now melted also at 150°. The prisms were dried at 100° for analysis.

0.1587 gram substance gave 0.2548 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2\ C_5H_{11}OH$.	Found.
Br	68.34	68.29

The α-isoamyl compound crystallizes in bright-yellow prisms, but, as mentioned in the preceding paragraph, it also occurred in rosettes showing a different crystalline habit, perhaps a different crystalline form. It is possible, therefore, that it is dimorphous, but it seems more probable that the formation of the rosettes was due to a trace of some impurity, which modified the habit of the crystals. This view receives a certain amount of support from the fact that the crude product was converted by ethyl alcohol, either hot or cold, into the hexabromorthoquinopyrocatechine ether, $C_6Br_4O_2C_6Br_2O_2$, recognized by its bright-red color, insolubility in the common solvents, infusibility below 300°, and the characteristic red prisms, obtained on crystallizing it from nitrobenzene. After one crystallization from ligroin the crude product still showed this behavior with ethyl alcohol, but not after two crystallizations. It is possible that the impurity, which caused the formation of the ether, was also responsible for the appearance of the rosettes. Similar cases of the formation of the ether from crude products by the action of alcohol have been observed in this laboratory, especially in the product of the action of acetic acid on the tetrabromorthoquinone.

The α-isoamyl alcohol compound melts at 150°, giving a yellow liquid, and in this respect differs from the other compounds of the α-series, which turn red when they melt. This difference is, however, more apparent than real, since this substance, if heated to a higher temperature, turns red and at 190° is converted into a red solid. It is evident, therefore, that the melting-point of the isoamyl compound lies below the point of decomposition, whereas the higher melting-points of the other α-bodies known lie above this point. In solubilities the isoamyl body resembles the other α-compounds, except that it is more soluble than they are in ligroin, which is the best solvent for it.

β-Isoamyl Alcohol Tetrabromorthoquinone, $(C_6Br_4O_2)_2.C_5H_{11}OH$.—This substance was prepared by treating the α-compound with dilute sodic hydrate, as described under the other β-bodies. After recrystallization from benzene and alcohol it showed the constant melting-point 177°, when it was dried at 100° and analyzed.

0.1568 gram substance gave 0.2531 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.C_5H_{11}OH$.	Found.
Br	68.34	68.69

It crystallizes in small, white prisms melting at 177° and resembles the other β-compounds in solubility.

Action of Tertiary Butyl Alcohol on Tetrabromorthoquinone.

Five grams of tetrabromorthoquinone were mixed with 10 cc. of the alcohol and allowed to stand in a corked flask. The action was much slower than with the other alcohols studied, but after 3 days some small, white prisms appeared. As the alcohol usually solidified over night, it was necessary to warm the mixture to melt it, but even this did not make the reaction run so fast as in other cases. After 4 weeks the orange-red, crystalline product was washed with a mixture of 1 part of benzene to 2 of ligroin and then recrystallized from a mixture of equal parts of these solvents, but the product was not homogeneous, since it consisted of yellow needles and short, red prisms. Unfortunately, the amount of the tertiary alcohol at our disposal was too small to allow us to make a further study of this product.

Reduction of the α-Methyl Alcohol Compound, $(C_6Br_4O_2)_2.CH_3OH$.

Five grams of the substance, mixed with a large excess of granulated zinc and 50 cc. of 95 per cent acetic acid, were heated on the steam-bath until the reaction started, and then allowed to stand at ordinary temperatures. The liquid turned dark-brown and the undissolved α-compound took on a slightly reddish color. After about 5 minutes light-brown needles began to separate from the solution, but the reaction was not complete until the mixture had stood 4 or more days. The action ran much faster when the flask was heated, but as this gave a less pure product, we found it wiser to carry on the reduction in the cold. After the α-compound had disappeared, the brown needles were filtered out and washed first with dilute acetic acid, and afterward with warm water. The crude product, which melted at 265°–270°, was recrystallized from benzene until it showed the constant melting-point 274°–275°, when it was dried at 100° and analyzed:

I. 0.2227 gram substance gave, on combustion, 0.1853 gram CO_2 and 0.0113 gram H_2O.

II. 0.2552 gram substance gave 0.2142 gram CO_2 and 0.0133 gram H_2O.

III. 0.1665 gram substance gave, by the Carius method, 0.2630 gram AgBr.

IV. 0.1594 gram substance gave 0.2525 gram AgBr.

V. 0.2079 gram substance gave 0.3292 gram AgBr.

	Calculated for $C_{18}Br_8O_6H_4$.	Found.				
		I.	II.	III.	IV.	V.
C	22.59	22.69	22.90	. .	. .	. .
H	0.42	0.57	0.58	. .	. .	. .
Br	66.94	. .	. .	67.22	67.41	67.38

Porter found 67.40 per cent of bromine in the product obtained by reducing the α-benzyl alcohol compound. The results obtained agree better with the formula $C_{18}Br_8O_6H_2$ than with that given, but as the study of the acet and benzoyl derivatives shows that it contains three hydroxyl groups, the formula with 4 atoms of hydrogen must be adopted.

The filtrate from this reduction-product had a beautiful purplish-red color, but we found the organic compound it contained very unmanageable, since, on spontaneous evaporation, it gave a tar (with which ferric chloride produced a dark-green solution, indicating the presence of a pyrocatechin), while the addition of a large quantity of water threw down a flocculent white precipitate, which gradually turned brown. In the filtrate from this we obtained a good test for a bromide with argentic nitrate and nitric acid.

Reduction of Other α-Bodies.

The reduced methyl compound described above resembles closely the reduction-product from the α-benzyl compound prepared by Porter and one of us,[1] which was described as having a pale straw color and melting at 273°–274°. To make sure they were identical, the reduction was repeated with 2 grams of the α-benzyl alcohol body, $(C_6Br_4O_2)_2.C_7H_7OH$, an excess of granulated zinc and 20 cc. of 95 per cent acetic acid. The reaction ran more slowly than with the methyl compound and it was found necessary to heat the mixture frequently in order to make the reduction complete. At the end of 6 days brown needles were obtained, which, after crystallization from benzene, showed the constant melting-point 274°–275°, and coincided in every respect with the product from the methyl alcohol body.

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[1] This Journal, 31, 105 (1904).

The α-water compound, $(C_6Br_4O_2)_2.H_2O$ (made by the action of ordinary toluene on tetrabromorthoquinone), was also reduced. The preparation of this water compound ran much more slowly than before, occupying 4 weeks instead of 1. This was probably due to the presence of less moisture than usual in the specimen of toluene used. When reduced as in the previous cases, the liquid became yellowish-brown and brown needles were deposited at once. The reaction seemed to be complete after standing for a few hours at ordinary temperatures (it was started by gentle heating), but the mixture was allowed to stand a day for greater certainty. This reduction, therefore, is much more rapid than that of the alcohol compounds. The product, after crystallization from benzene, melted constantly at 274°–275° and was identical with the others. The filtrate from the brown crystals was colorless, while the alcohol compounds gave a reddish-purple filtrate. It contained bromide.

The red methyl alcohol compound, $(C_6Br_4O_2)_4.CH_3OH$, when reduced with zinc and acetic acid, yielded the same product melting at 274°–275°. In this case the reduction seemed to be complete after 3 days, but the mixture was allowed to stand 4.

Properties of the Reduced α-Bodies. Octobromdihydroxyhemipyrocatechinepyrocatechine Ether.—It crystallizes from benzene in small, light-brown prisms with a characteristic silky luster, which unite to form large, compact leaves. It melts at 274°–275° and is insoluble in most of the organic solvents when cold, only slightly soluble in them when boiling. It is, however, fairly soluble in boiling benzene or acetone and readily soluble in boiling nitrobenzene. Hot sulphuric acid or hydrochloric acid has no action on it; nitric acid converts it into a red product melting at 295°, described later. Sodic hydrate turns it to a purple substance. Acetic anhydride and sodic acetate give acet compounds, described in the next section.

Action of Acetic Anhydride on the Octobrom Reduction-product.—One gram of the reduction-product, mixed with 1 gram of dry sodic acetate, was boiled with 20 cc. of acetic anhydride until it dissolved, which usually took about 5 minutes, and the product was then precipitated with water. The products from different preparations varied in melting-points from 265°–270° to 280°–285°, and from white to pale-brown in color. All of them together were recrystallized from a mixture of 2 parts of benzene with 1 of alcohol, until two different bodies were isolated, one of which melted constantly at 304°–305° and proved to be the diacet compound, the other, melting constantly at 273°–275°, was the triacet compound. Analysis of the substance melting at 304°–305°, dried at 100°:

0.1576 gram substance gave 0.2292 gram AgBr.

	Calculated for $C_{18}Br_8O_6(COCH_3)_2H_2$.	Found.
Br	61.54	61.87

Properties of the Diacet Compound.—It crystallizes in small prisms of a brownish- or yellowish-white color, which melt at 304°–305°. It is soluble in chloroform or carbonic disulphide; slightly soluble in cold benzene or acetone, soluble when hot; essentially insoluble in alcohol, ether, glacial acetic acid or ligroin. It is not acted on by the three strong acids or by sodic hydrate.

Analysis of the substance melting at 273°–275°, dried at 100°:

I. 0.1581 gram substance gave 0.2191 gram AgBr.
II. 0.1529 gram substance gave 0.2120 gram AgBr.

	Calculated for $C_{18}Br_8O_6(COCH_3)_3H$.	Found.	
		I.	II.
Br	59.15	58.95	59.00

Porter[1] analyzed the same substance and obtained 59.29 per cent of bromine.

This triacet compound melts constantly at 273°–275° and, in appearance and solubilities, resembles the diacet body.

These results were confirmed by some experiments on the action of benzoyl chloride with the reduction-product. The action of these substances gave a product which melted constantly at 250°–255° after purification, and further treatment with benzoyl chloride altered neither the melting-point nor the composition. It was dried at 100° for analysis. Analysis II. was made with a sample which had been treated a second time with benzoyl chloride.

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[1] This Journal, **31**, 106 (1904).

I. 0.1650 gram substance gave 0.1922 gram AgBr.
II. 0.1618 gram substance gave 0.1880 gram AgBr.

	Calculated for $C_{18}Br_8O_6(C_6H_5CO)_3H$.	Found. I.	II.
Br	50.46	49.56	49.45

These results indicate that the substance is a slightly impure tribenzoyl compound, which is confirmed by the somewhat indefinite melting-point. Unfortunately, lack of time prevented us from preparing a pure specimen.

In one preparation a different substance, melting at 285°–287°, was obtained, but in too small quantity for analysis.

Oxidation of the Reduction-Product.

Our experiments on this subject were not brought to an end, owing to the departure of one of us from Cambridge, but we think them of sufficient interest for publication even in this unfinished state.

When 0.5 gram of the reduced α-substance were mixed with 5 cc. of glacial acetic acid and treated with 1 cc. of fuming nitric acid of sp. gr. 1.50, the brown color of the original substance immediately changed to red. After 2 or 3 minutes a large quantity of water was added, the mixture thoroughly stirred, the precipitate filtered out, washed free from acid and dried at 100° for analysis (I.). The yield was quantitative. The same product was obtained by warming the reduction-product on the steam-bath with ordinary strong nitric acid. This was also dried at 100° for analysis (II.) :

I. 0.1625 gram substance gave 0.2575 gram AgBr.
II. 0.1631 gram substance gave 0.2588 gram AgBr.

	Calculated for $C_{18}Br_8O_6H_2$.	Found. I.	II.
Br	67.09	67.44	67.51

This red product melted at about 295°, but it was shown to be a mixture by extracting it with boiling chloroform, when four successive extracts melted as follows :

I.	275°–280°
II.	275°–280°
III.	280°–285°
IV.	285°–287°

These extracts consisted of small, red prisms mixed with a few pale-yellow needles. The residue, which had melted throughout this extraction at 290°–293°, was then treated with boiling chloroform in a continuous extracter, when orange needles were obtained which did not melt below 310°. The red prisms could not be converted into the yellow needles by boiling for half an hour with chloroform, or by any other method we have found as yet. The quantities of these two bodies were not enough for purification and analysis, but the work will be repeated in the near future, on a larger scale, in this laboratory.

A curious phenomenon was observed when the crude reduction-product of the α-bodies was boiled with alcohol or benzene, as it was converted into a substance with a striking pale-lilac color. This change did not take place if the purified reduction-compound was used. We thought, therefore, that it was probably due to the zincic acetate left from the reduction, and upon boiling the pure reduction-product with alcohol and sodic acetate or zincic chloride we obtained, in each case, the same pale-lilac substance. It turned brown at about 200°, but did not melt below 310° ; it was essentially insoluble in water or most of the organic solvents ; only slightly soluble in toluene or nitrobenzene, even when boiling. Hydrochloric acid converted it into a brown product. Nitric acid turned it red. Acetic anhydride and sodic acetate dissolved it and the brown product formed melted at 270°–273°. Owing to the difficulty of purifying this substance, we were unable to get satisfactory analytical results in the time at our disposal and therefore postpone the discussion of its nature until a sufficient number of data have been collected.

Reductions of the tetrabrompyrocatechine and of the hexabromorthoquinopyrocatechine ether with zinc and acetic acid were studied, in the hope that they might throw some light on the reduction of the α-compounds. The same product was obtained in each case, that is, hexabromdihydroxypyrocatechine ether more or less impure. The product from the ether gave, with alcohol, a purple substance similar in appearance to that described in the last paragraph, but we think it is a different body from a study of its other properties.

Experiments with the β-Compounds.

Five-tenths of a gram of the β-benzyl alcohol compound, $(C_6Br_4O_2)_2.C_7H_7OH$, mixed with 0.5 gram dry sodic acetate, was boiled for 15 minutes with 5 cc. of acetic anhydride and then the brownish solution was precipitated with water. The light-brown, flaky product was recrystallized from a mixture of 1 part of benzene and 3 of methyl alcohol, until it showed the constant melting-point 210°, when it was dried at 100° for analysis :

0.1591 gram substance gave 0.2373 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2C_7H_7OCOCH_3$.	Found.
Br	64.13	63.46

Properties of the Acetbenzylalcohol Tetrabromorthoquinone.—It crystallizes from a mixture of benzene and methyl alcohol, or of chloroform and common alcohol in small, white needles. It melts at 210° and is freely soluble in ether, chloroform, benzene, acetone, or carbonic disulphide ; nearly insoluble in alcohol, glacial acetic acid or ligroin when cold, moderately soluble when hot ; essentially insoluble in water. The three strong acids have no perceptible action on it, and the same is true of sodic hydrate.

If the action of acetic anhydride on the β-benzyl alcohol body is continued for 6 hours a dark, charred mass was obtained, from which a mixture of benzene and methyl alcohol extracted a few brown needles melting, after one recrystallization, at 190°-195°.

Sulphuric acid of sp. gr. 1.44 did not affect the β-benzyl compound. It was decomposed by acid of sp. gr. 1.65, giving a brown product, which did not melt below 300° and turned red when treated with nitric acid.

Aniline dissolved the β-benzyl compound when warmed with it, but after removing the aniline with dilute hydrochloric acid the unaltered β-compound was recovered, as shown by the melting-point, 213°–215°.

The β-benzyl compound was unaffected by 3 per cent sodium amalgam, or by tin and hydrochloric acid. The β-methyl compound was converted into a black product by tin and hydrochloric acid and was slowly dissolved (on standing 2 weeks) by zinc and acetic acid.

The β-benzyl compound was recovered unaltered after boiling for an hour and a half with 5 grams of potassic dichromate, 5 cc. of sulphuric acid and 10 cc. of water. It was completely decomposed when strong sulphuric acid was used instead of dilute. The β-methyl compound behaved in the same way with these mixtures. With boiling, fuming nitric acid its color changed at first from white to green and later it was entirely decomposed. It was not affected by boiling with common strong nitric acid.

CAMBRIDGE, MASS.,
May 26, 1905.

Contributions from the Chemical Laboratory of Harvard College.

ADDITION-COMPOUNDS OF QUINONES AND TERTIARY AMINES.[1]

BY C. LORING JACKSON AND LATHAM CLARKE.

We were led to the study of the action of dimethylaniline on quinones by an experiment with tetrabromorthobenzoquinone, $C_6Br_4O_2$, which formed part of the extended study of this body now in progress in this laboratory. The strongly colored, unstable product of this reaction seemed so interesting that we tried to obtain similar compounds from other quinones and found that the reaction was one of general application. So far as we have been able to find, the only addition-compounds of amines and quinones, previously made, are those of various quinones with nitranilines discovered by Heberand[1] and Niemeyer,[2] but most of these contain 2 molecules of the amine to 1 of the quinone, whereas all of our compounds, which were analyzed, contained 1 molecule of each substance. There is some question, therefore, whether they belong to the same class.

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Latham Clarke.

The strong similarity in properties between the products from quinone and those obtained by the action of dimethylaniline on trinitrobenzene and related bodies led us to include these in our field of work, but after a preliminary paper[3] had been published we found, to our mortification, that we were intruding on an investigation reserved by Professor Sudborough[4] and have, consequently, confined our work after this to the compounds from quinones.

Dimethylaniline gave colored compounds with all the true quinones at our disposal. All of these were unstable, but we succeeded in isolating and analyzing the products from tetrabromorthobenzoquinone, $C_6Br_4O_2$, tetrachlorparabenzoquinone, $C_6Cl_4O_2$, trichlorparabenzoquinone, $C_6HCl_3O_2$, tetrabromparabenzoquinone, $C_6Br_4O_2$, and trichlortoluquinone, $CH_3C_6Cl_3O_2$, which were made up of 1 molecule of the quinone combined with 1 molecule of dimethylaniline. The compound with chloranil may be taken as an example. Its formula is

$$C_6Cl_4O_2C_6H_5N(CH_3)_2,$$

and it forms shining prisms of an intense indigo-blue color, which melt at 105°. The substance is so unstable that special precautions[5] must be taken to insure a good melting-point or analysis. When exposed to the air it loses dimethylaniline rapidly and after a day only the pure chloranil is left. This, however, is one of the more stable of these bodies, as many of them could not be obtained in crystals at all, but their formation was inferred from the very marked colors produced on mixing the components.

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[1] Ber. d. chem. Ges., **15**, 1976 (1882).

[2] Ann. Chem. (Liebig), **228**, 322 (1885).

[3] Ber. d. chem. Ges., **37**, 176 (1904).

[4] J. Chem. Soc., **79**, 522 (1901) ; **83**, 1334 (1903).

[5] Given under chloranil in the experimental part.

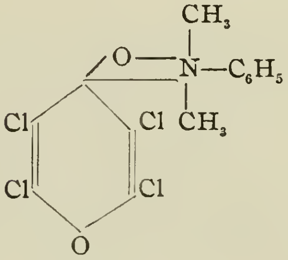
Similar results were obtained with other amines belonging to several different classes, and analyses were obtained of the more important derivatives of dimethylparatoluidine, which also were made up of 1 molecule of each constituent. With the other amines the formation of a compound was inferred from the appearance of a color, but care was taken to distinguish between the colors caused by these unstable addition-compounds and those due to the formation of a stable coloring-matter.

If these addition-compounds do not belong to the ill-defined class of molecular compounds, but their constituents are united to form a single molecule (which is not established), our experiments lead to the following, more or less probable, conclusions in regard to their structure :

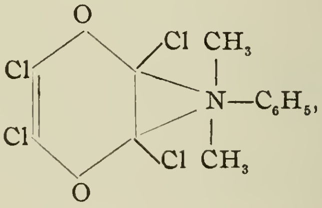
The amines must be united to the quinones by the nitrogen, which thus becomes quinquivalent, because colors were obtained from dimethylaniline, monomethylaniline, parabromdimethylaniline, dibromdimethylaniline, dimethyltoluidines, dimethylnaphthylamines, diethylnaphthylamines, dimethylbenzylamine, dimethylisoamylamine, α-naphthylamine, tetramethyldiaminotriphenylmethane, diphenylamine and pyridine ; and these substances have only one point in common, they all contain trivalent nitrogen and have, therefore, two affinities of the nitrogen free, ready for use in joining them to other bodies.

On the other hand, no colored compounds could be obtained from trimethylphenylium bromide, $C_6H_5N(CH_3)_3Br$, or iodide, and only traces of color were seen with the hydrobromide of dibromdimethylaniline, $C_6H_3Br_2N(CH_3)_2HBr$, just enough to be caused by a partial dissociation of the salt. The one fact observed by us, which is not in harmony with this conclusion, is the absence of color in experiments with tribenzylamine. This may be explained by the occupation of the space about the atom of nitrogen by the large benzyl molecules, which might prevent the action of its additional affinities, when the smaller methyl groups would have no such action, but much more experimental work is needed before this explanation can-be accepted with certainty and, in the meantime, the force of this objection to our conclusion must not be underestimated. We hope to undertake experiments in this direction in the near future.

The interpretation of our experiments is much more difficult, when we try to determine in what way the quinone is joined to the amine. That the formation of addition-compounds depends on the quinone structure seems to be established by the fact that colors were obtained from parabenzoquinone, $C_6H_4O_2$, and its derivatives (monochlorquinone, dichlorquinone, trichlorquinone, chloranil, bromanil, dibromquinone, dichlordimethoxy- or diethoxyquinone), from tetrabrom- or tetrachlororthobenzoquinone, from toluquinone and trichlortoluquinone, from dibromthymoquinone, from 1,4-naphthoquinone and from anthraquinone. On the other hand, no colors could be obtained from hydroquinones or pyrocatechins (tetrachlorhydroquinone, dichlordiisoamyloxyhydroquinone, dichlordibenzyloxyhydroquinone, or tetrabrompyrocatechine). The most probable ways in which the amine would be connected with the quinone would be either at the oxygen atoms or at the sides of the benzene ring; these two configurations are represented for the compound of chloranil and dimethylaniline by the following formulas,

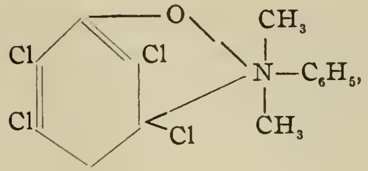


I.



II.

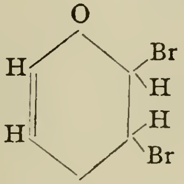
both of which look decidedly strange. The only other alternative would be that the addition took place partly on the ring and partly through the oxygen,

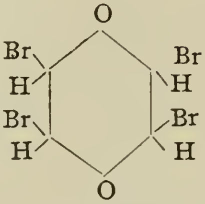


III.

which seems even more improbable.

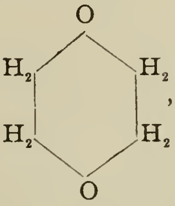
The experiments for determining which of these formulas is the most probable consisted (1) of those with compounds composed of saturated rings with atoms of oxygen in the quinone position, (2) of those with the oxygen atoms of the quinone modified. To the first class belonged our work with Nef's bromides of quinone.





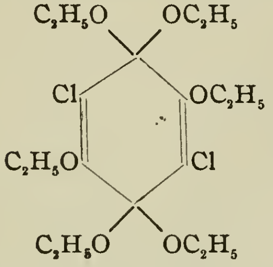
With the dibromide, colors were obtained with dimethylaniline; but the tetrabromide, in chloroform solution, gave at first no color and although, on standing, a coloration gradually appeared, we proved that this was accompanied by a splitting off of hydrobromic acid to form a substituted quinone.

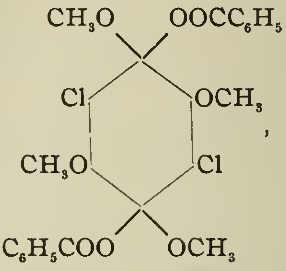
The paradiketohexamethylene,



also gave no reaction with dimethylaniline. It would seem, therefore, that an unsaturated ring is necessary for the formation of these addition-compounds.

Compounds with both quinone atoms of oxygen modified, such as dichlordiethoxyquinone tetraethylacetal and dichlordimethoxyquinone dibenzoyldimethylacetal,



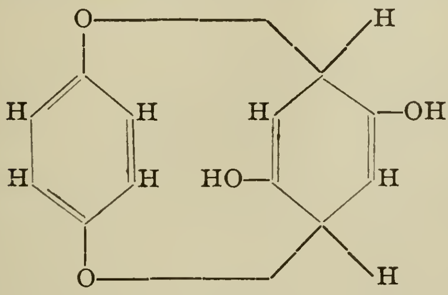


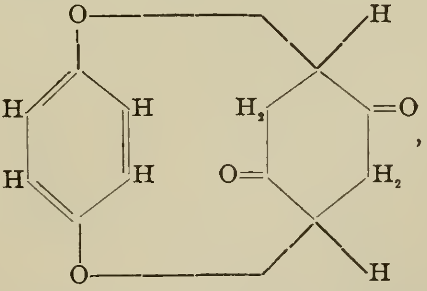
gave no colors whatever; and, while the quinone monoxime and dichlorquinone monoxime gave colors, no colors could be obtained from the corresponding dioximes.

These results would seem to point to the necessity of both an unsaturated ring and a quinone oxygen atom for the formation of the addition compounds—conditions which indicate the structure given in Formula III; but such an improbable constitution should not be adopted without convincing proof, and this is not given by our experiments, as is shown by the following discussion: The indifference of the dioximes might be explained by the reduction of the negative properties of the quinone, since it was found that the strongly negative derivatives of quinone formed more stable products than those which were more positive, for instance, the compounds obtained from trichlorquinone were found to be more stable than those from quinone in seven cases. It was observed, also, that the presence of large radicals attached to the quinone was unfavorable to the formation of our compounds. Thus dichlordiethoxyquinone, or dichlordimethoxyquinone, gave very unstable compounds, while the corresponding isoamyl and phenyl derivatives gave none at all. As, then, the dichlordimethoxyquinone barely forms these compounds, it is not surprising that the acetals mentioned above should refuse to act. These considerations weaken the force of the objections to Formula II. so much that it would not be wise to reject it.

On the other hand, the arguments against Formula I. are but little weakened by a similar discussion, as the paradiketohexamethylene can hardly be so much more positive than quinone as to owe its indifference to this cause, and the presence of the bromine in the tetrabromide is not likely to prevent the formation of a compound, when bromanil forms a decidedly stable one.

We have left, therefore, Formula III., which is in harmony with all the observed facts, and Formula II., which can be brought into harmony with them with some little difficulty. Nevertheless, Formula II. may be more probable than III., as the latter represents an unusual form of addition, whereas II. suggests a relationship with quinhydrone, which Posner[1] has recently proved has one or the other of these formulas,





and our addition compounds show a most striking similarity to quinhydrone in composition and in their marked colors and instability.

Although, as already stated, trichlorquinone, owing to its negative properties, gave more stable bodies than quinone itself, it was a curious observation that tetrachlorquinone, in four cases, seemed to give less stable products than trichlorquinone. Perhaps this may be due to steric effects. Trichlortoluquinone seemed to behave, in this respect, like trichlorquinone. Too much weight, however, must not be given to these observations, as they are somewhat indefinite.

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[1] Ann. Chem. (Liebig), **336**, 90 (1904).

It is, perhaps, worth mentioning that in the addition-compounds from dimethylaniline the presence of halogen in the quinone tends to impart a blue color to the substance ; all those containing 2 or more atoms of halogen are blue or purple, those with 1 atom of halogen, or none at all, are red. The same rule applies to some, but not to all of the other amines studied.

EXPERIMENTAL.

Tetrabromorthoquinone and Dimethylaniline, $C_6Br_4O_2C_6H_5N(CH_3)_2$.—The tetrabromorthobenzoquinone was prepared by the method of Zincke[1] and melted at 150°–151°. The addition-compound is so unstable that it can be obtained, successfully, only by careful attention to the following conditions. One-half gram of the tetrabromorthoquinone, dissolved in 20 cc. of alcohol, was mixed, as rapidly as possible, with a solution of 0.5 gram dimethylaniline in 10 cc. of alcohol. A greenish color appeared at once and, after the sides of the beaker had been rubbed briskly with a glass rod, a purple precipitate was deposited in about 5 seconds. This was filtered off as quickly as possible, using a large funnel and perforated plate with the filter-pump. If the filtering lasted more than a few seconds the precipitate disappeared, forming a yellowish-brown solution. The crystals were dried rapidly by pressure on filter-paper and analyzed :

0.0528 gram substance gave, by the Carius method, 0.0720 gram AgBr.

	Calculated for $C_6Br_4O_2C_6H_5N(CH_3)_2$.	Found.
Br	58.68	57.98

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[1] Ber. d. chem. Ges., 20, 1777 (1887).

The substance, therefore, contains 1 molecule of each constituent.

The addition-compound of tetrabromorthoquinone and dimethylaniline forms fine, glistening, purple needles, which are so unstable that they are converted into a black wax in 3-5 minutes at ordinary temperatures, but keep somewhat longer if artificially cooled. In contact with alcohol the substance is decomposed even more rapidly.

Tetrachlororthobenzoquinone gave a similar result with dimethylaniline, but as the addition-product seemed to be even less stable than the tetrabrom body, no attempt was made to study it. Tetrabrompyrocatechine did not react with dimethylaniline.

Chloranil and Dimethylaniline, $C_6Cl_4O_2C_6H_5N(CH_3)_2$.—The tetrachlorparabenzoquinone used in this work was first carefully freed from trichlorquinone. The chloranil was dissolved in a little dimethylaniline and to the strong solution thus obtained, four times its volume of alcohol were added after a few minutes. Beautiful, blue crystals of the product separated, usually at once, or occasionally after the lapse of a few minutes. A more dilute solution gave very handsome, large crystals after standing for some hours, but we preferred to prepare it from the more concentrated solutions for fear that the substance might be partly decomposed by long standing with the solvent. It was dried for analysis by rapid pressing on filter-paper.

0.1290 gram substance gave, by the Carius method, 0.2018 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6H_5N(CH_3)_2$.	Found.
Cl	38.64	38.68

It crystallizes in slender, blunt-ended prisms of a dark, intense blue color with a bronze reflex. It melts at 105°. In taking the melting-points of these substances the specimen should be freshly prepared and kept moist with dimethylaniline until the moment of taking the melting-point ; it is then dried on filter-paper as rapidly as possible and put at once into the melting-tube. With these precautions very constant results were obtained in spite of the great ease with which these compounds decompose. This body decomposes rapidly on exposure to the air, the dimethylaniline evaporating off. The decomposition begins as soon as the substance is exposed to the air, becomes very evident in the first half hour and after standing for less than a day all the dimethylaniline has evaporated and pure chloranil is left. When the crystals are covered with ether, chloroform, acetone, or ligroin the color changes in a few moments to green, or even yellow, from the extraction of the loosely combined dimethylaniline; alcohol gives a more stable, blue solution with it, especially if some dimethylaniline is present.

The mineral acids decolorize the crystals almost instantly with the formation of salts of the dimethylaniline. When heated to temperatures above its melting-point, the substance is converted into a dark blue product, undoubtedly identical with the coloring-matter described by Greiff,[1] patented by Meister Lucius and Brüning[2] and investigated by Wichelhaus.[3]

Trichlorparabenzoquinone and Dimethylaniline, $C_6HCl_3O_2C_6H_5N(CH_3)_2$.—This substance was obtained in just the same way as that from chloranil. It was dried rapidly on filter-paper and analyzed.

0.2037 gram substance gave, by the Carius method, 0.2535 gram AgCl.

	Calculated for $C_6HCl_3O_2C_6H_5N(CH_3)_2$.	Found.
Cl	32.03	30.76

It crystallizes in beautiful, slender prisms with blunt ends made up of four or more plates. It is dark blue with a bronze reflex and melts at 65°. It loses dimethylaniline on exposure to the air and is decolorized instantly by chloroform or the mineral acids. Alcohol decomposes the substance in a short time, unless it contains dimethylaniline, which renders the solution more stable. It dissolves without apparent decomposition in ether, benzene, or acetone.

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[1] Ber. d. chem. Ges., **12**, 1610 (1879).

[2] *Ibid.*, **13**, 212, 2100 (1880).

[3] *Ibid.*, **14**, 1952 (1881).

2,5-Dichlorparabenzoquinone and Dimethylaniline.—The dichlorquinone, prepared according to the method of Ling,[1] showed the melting-point 161°. It was dissolved in twice its weight of dimethylaniline, when a deep blue color appeared instantly, but the addition compound was not easy to obtain in the solid state. We finally accomplished this by allowing the solution in dimethylaniline to stand exposed to the air for several hours, when a network of very slender, deep blue needles was deposited. If the solution was allowed to stand too long another purple crystalline body separated, which was much more stable than the original addition-compound, as it dissolved unchanged in alcohol and even underwent boiling of this solution without any change of color. It is probably a coloring-matter similar to that obtained from the chloranil body. The addition-compound was rapidly decomposed, even in the cold, by all the solvents we have tried.

Chlorquinone, prepared by the method of Levy and Schultz,[2] gave, at once, a reddish-violet color with dimethylaniline and the addition of ether precipitated a dark red oil, which we have not succeeded in converting into a solid product. Quinone also gave a dark red color with dimethylaniline, but all our attempts to isolate a solid product failed. Alcohol gave a red oil; other solvents, as a rule, discharged the color. This color reaction can be obtained with very small amounts of either substance, so that it can be used as a test for a quinone or a dialkylamine.

Bromanil and Dimethylaniline, $C_6Br_4O_2C_6H_5N(CH_3)_2$.—The tetrabromparabenzoquinone was dissolved in a small quantity of dimethylaniline and, on standing, the addition-compound was deposited from the deep blue solution. It was dried for analysis by pressure with filter-paper.

0.4362 gram substance gave 0.6030 gram AgBr.

	Calculated for $C_6Br_4O_2C_6H_5N(CH_3)_2$.	Found.
Br	58.71	58.81

It forms a purple powder, which, under the microscope, appears as a network of fine, purple needles. It melts at 65°–68° ; no sharper melting-point could be obtained. It is decomposed by solvents or the mineral acids.

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[1] J. Chem. Soc., **61**, 558 (1892).

[2] Ann. Chem. (Liebig), **210**, 138 (1881).

Trichlortoluquinone and Dimethylaniline, $CH_3C_6Cl_3O_2C_6H_5N(CH_3)_2$.—Trichlortoluquinone, prepared according to Elbs and Brunschweiler,[1] gave a deep blue solution with dimethylaniline, which deposited, on standing, purple needles of the addition-compound.

0.1366 gram substance gave 0.1668 gram AgCl.

	Calculated for $CH_3C_6Cl_3O_2C_6H_5N(CH_3)_2$.	Found.
Cl	30.58	30.18

It is obtained by the spontaneous evaporation of its alcoholic solution in beautiful, flat, purple prisms, which melt at 68°–73° and dissolve, without apparent decomposition, in alcohol, benzene, or acetone.

Toluquinone, made by Clark's method,[2] gave a red solution with dimethylaniline, from which 90 per cent alcohol precipitated a red oil. Dibromthymoquinone gave a purple solution with dimethylaniline, from which dilute alcohol precipitated a purple oil that dissolved, with loss of color, in alcohol, ether, or benzene, but on evaporation of the solvent the color returned. Dichlordiethoxyquinone[3] also gave a reddish-purple color with dimethylaniline, but not even a colored oil could be obtained from the solution. Both 1,4-naphthoquinone[4] and anthraquinone gave a red color with dimethylaniline.

Bromides of Quinone and Dimethylaniline.

Nef's quinone dibromide,[5] $C_6H_4Br_2O_2$, gave, with dimethylaniline, a blue paste, from which we did not succeed in isolating a solid compound. It dissolved in alcohol, ether, or acetone without loss of color and is, therefore, decidedly stable for a substance of this class.

Quinone tetrabromide[6] gave a blue color at once with dimethylaniline, but, if the bromide was dissolved in chloroform, no color appeared until the mixture had stood for some time and the gradual formation of color after this was associated with the removal of hydrobromic acid, as proved by the following experiment:

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[1] J. prakt. Chem., [2], **52**, 559 (1895).

[2] THIS JOURNAL, **14**, 555 (1892).

[3] *Ibid.*, **17**, 605 (1895).

[4] Made by the method of Japp and Miller. J. Chem. Soc., **39**, 220 (1881).

[5] J. prakt. Chem., [2], **42**, 182 (1890).

[6] *Ibid.*, [2], **42**, 182 (1890).

Two-tenths of a gram of quinone tetrabromide were dissolved in 10 cc. of pure, dry chloroform and 0.2 gram of dimethylaniline added. The solution remained colorless and a test for hydrobromic acid gave a negative result. To make the test a small portion of the mixture was withdrawn, shaken with water and the aqueous extract treated with a drop of nitric acid and argentic nitrate. These tests were repeated at intervals of 5 minutes and gave negative results until the fourth time; then a slight trace of hydrobromic acid was detected and at the same time there appeared a faint blue color in the mixture. After another minute this color had become distinctly marked and a considerable amount of hydrobromic acid was present, while at the end of the fifth 5-minute period the color was very deep and the test for hydrobromic acid very strong. Such experiments have been repeated several times with the same result and it was found that the time of the appearance of the color and the test for hydrobromic acid did not differ more than 3 minutes in the several trials. With half the concentration of the solution of quinone tetrabromide the time before the appearance of the color and hydrobromic acid was longer, and, with double the concentration, it was reduced from about 20 to about 16 minutes.

The formation of hydrobromic acid, parallel with the appearance of the color, in all these experiments shows that the tetrabromide does not react with the dimethylaniline but that the addition-product is formed from the substituted quinone, produced by the removal of hydrobromic acid (as hydrobromide of dimethylaniline) from the quinone tetrabromide.

Oximes of Quinone.

Paraquinone monoxime, prepared by the method of Bridge,[1] was dissolved in alcohol and dimethylaniline added to the clear, colorless solution; a red color appeared at once, but no compound fit for analysis could be isolated. The addition-compound was evidently decidedly unstable, as the solution yielded a yellowish-green tar on standing. Quinone dioxime, made according to Nietzki and Guiterman,[1] gave no color with dimethylaniline. 2,5-Dichlorquinone monoxime, made according to Kehrmann,[2] gave a strong red color with dimethylaniline, but no compound was isolated, as the solution gave a yellowish-green tar on standing. On the other hand, no color was obtained when the 2,5-dichlorquinone dioxime[3] was mixed with dimethylaniline.

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[1] Ann. Chem. (Liebig), **277**, 85 (1893).

The following compounds gave no change of color when mixed with dimethylaniline:

Paradiketohexamethylene,[4]

$$C_6H_8O_2;$$

dichlordiethoxyquinone tetraethylacetal,[5]

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4;$$

dichlordimethoxyquinone dibenzoyldimethylacetal,[6]

$$C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2(OCH_3)_2;$$

dichlordiisoamyloxyquinone,[7]

$$C_6Cl_2(OC_5H_{11})_2O_2;$$

dichlordiphenoxyquinone,[8]

$$C_6Cl_2(OC_6H_5)_2O_2;$$

dianilinobromquinoneanil,[9]

$$C_6HBr(C_6H_5NH)_2ONC_6H_5;$$

tetrachlorhydroquinone,

$$C_6Cl_4(OH)_2;$$

dichlordiisoamyloxyhydroquinone,[10]

$$C_6Cl_2(OC_5H_{11})_2(OH)_2;$$

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[1] Ber. d. chem. Ges., **21**, 429 (1888).

[2] *Ibid.*, **21**, 3319.

[3] Obtained as a secondary product in making the monoxime.

[4] Hermann: Ann. Chem. (Liebig), **211**, 321 (1882).

[5] Jackson and Grindley: THIS JOURNAL, **17**, 633 (1895).

[6] *Ibid.*, **17**, 643 (1895).

[7] Jackson and Oenslager: *Ibid.*, **18**, 9 (1896).

[8] Jackson and Grindley: *Ibid.*, **17**, 595 (1895).

[9] Jackson and Porter: *Ibid.*, **30**, 531 (1903).

[10] Jackson and Oenslager: *Ibid.*, **18**, 10 (1896).

dichlordibenzyloxyhydroquinone,[1]

$$C_6Cl_2(OC_7H_7)_2(OH)_2.$$

Experiments with Derivatives of Dimethylaniline.

Parabromdimethylaniline[2] gave a red color with quinone, a blue color with trichlorquinone. Dibromdimethylaniline[3] gave a red color with quinone; with trichlorquinone a violet color. The hydrobromide of dibromdimethylaniline,

$$C_6H_3Br_2N(CH_3)_2HBr,$$

gave a slight red color after it had stood a few minutes with trichlorquinone, in alcoholic or benzene solution. The color was obviously due to a slight decomposition of the salt into hydrobromic acid and free dibromdimethylaniline. Trimethylphenylium bromide, $C_6H_5N(CH_3)_3Br$, or the iodide, gave no color reaction with either quinone or trichlorquinone.

Experiments with Dimethyltoluidines.

The dimethylparatoluidine and dimethylorthotoluidine were prepared by the method[4] contrived by one of us.

Chloranil and Dimethylparatoluidine, $C_6Cl_4O_2C_6(CH_3)H_4N(CH_3)_2$.—One and two-tenths grams of tetrachlorparabenzoquinone were dissolved in 0.8 gram of the dimethyltoluidine and the pale blue solution thus obtained allowed to stand until it deposited crystals of the addition-product, which were dried on filter-paper for analysis:

0.2881 gram substance gave 0.4338 gram AgCl.

	Calculated for $C_6Cl_4O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Cl	37.10	37.22

It forms blue crystals, which give a violet powder and on standing in the air are converted into a green wax. It melts at 114° and is sparingly soluble in alcohol or acetone.

Trichlorquinone and Dimethylparatoluidine, $C_6HCl_3O_2C_6(CH_3)H_4N(CH_3)_2$.—A saturated solution of trichlorquinone in the dimethylparatoluidine, was allowed to stand for an hour and then mixed with its own volume of alcohol, when the addition-compound soon crystallized out. This body is very hard to obtain in a state of purity, because if the mixture stands too long before adding the alcohol it is converted into a black, sticky gum, and if, on the other hand, it does not stand long enough, the product is contaminated with unaltered trichlorquinone, which can be recognized by its yellow color. The pure compound was dried on filter-paper for analysis:

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[1] Jackson and Oenslager: THIS JOURNAL, **18**, 13 (1896).

[2] Weber: Ber. d. chem. Ges., 8, 715 (1875); **10**, 763 (1877).

[3] Fries: *Ibid.*, **37**, 2338 (1904).

[4] L. Clarke: THIS JOURNAL, **33**, 496 (1905).

0.2171 gram substance gave 0.2719 gram AgCl.

	Calculated for $C_6HCl_3O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Cl	30.58	30.96

It crystallizes in long, blue needles.

With dimethylparatoluidine, 2,5-dichlorquinone gave a deep blue color, monochlorquinone a light blue and quinone a brownish-red.

Trichlortoluquinone and Dimethylparatoluidine, $CH_3C_6Cl_3O_2C_6(CH_3)H_4N(CH_3)_2$.—The addition-compound was prepared by mixing its two constituents so as to make a concentrated solution, and adding to the deep blue liquid half its volume of alcohol. The substance crystallized out on standing and was dried on filter-paper for analysis:

0.2224 gram substance gave 0.2617 gram AgCl.

	Calculated for $CH_3C_6Cl_3O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Cl	29.54	29.08

It crystallizes in fine, deep blue needles and melts at 74°–76°. It is decolorized by solvents almost instantly.

Bromanil and Dimethylparatoluidine, $C_6Br_4O_2C_6(CH_3)H_4N(CH_3)_2$.—The product crystallized out from a concentrated solution of the tetrabromparabenzoquinone in the dimethylparatoluidine, after it had stood for about half an hour. It was dried on filter-paper.

0.2312 gram substance gave 0.3092 gram AgBr.

	Calculated for $C_6Br_4O_2C_6(CH_3)H_4N(CH_3)_2$.	Found.
Br	57.14	56.93

It forms pale blue crystals, melting at 109°, which are essentially insoluble in alcohol, but are partially decomposed by it.

Dimethylorthotoluidine.—No definite compounds were isolated with dimethylorthotoluidine, but the following color reactions were obtained: With chloranil a red color was formed, which was discharged by solvents; the addition-compound is very unstable, since unchanged chloranil separated on cooling a hot solution of this body in the dimethylorthotoluidine. With trichlorquinone it gave a deep violet-red color which, apparently, was not discharged by ether, benzene, or acetone. The liquid was partially decolorized by alcohol, completely by acetic acid. No definite compound could be isolated. With tetrabromquinone the dimethylorthotoluidine gave a violet color; with quinone a brownish-red color; with toluquinone a bright red; with trichlortoluquinone a deep red color; with dibromthymoquinone a bright red; with 1,4-naphthoquinone a light red color.

Experiments with Benzylamines.

The dimethylbenzylamine used in this work was prepared by the method contrived by one of us.[1] Trichlorquinone, if treated with pure dimethylbenzylamine, was converted at once into a reddish tar, but if the quinone was dissolved in twenty times its weight of ethyl acetate, or toluene, and the amine added to the solution, a beautiful bright red color was produced instantly and on rubbing the sides of the beaker with a glass rod tufts of red, microscopic crystals were deposited. All our attempts to analyze this substance failed, as the crystals melted down to a green wax before they could be removed from the beaker or dried.

Quinone dissolved in ethyl acetate gave a deep red color on the addition of dimethylbenzylamine. On evaporating off the solvent a dark red oil was obtained, which could not be brought to solidification, although it dissolved in benzene, acetone, or ether without change of color. Tribenzylamine, made by Mason's process,[2] gave no color reaction with any of the quinones at our disposal.

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[1] L. Clarke: THIS JOURNAL, 33, 496 (1905).

[2] J. Chem. Soc., 63, 1314 (1893).

Experiments with Dimethylisoamylamine.

The dimethylisoamylamine was made by the method contrived by one of us.[1] With trichlorquinone it gave a dark red color and, if the reaction took place in benzene solution and the sides of the beaker were rubbed with a glass rod, red crystals separated, which turned to a red wax in a few seconds, so that it was impossible to obtain an analysis or melting-point. Quinone gave a red color with the dimethylisoamylamine. If the reaction took place in benzene solution, a red oil was obtained by evaporation of the solvent, but it could not be brought into a state fit for analysis.

Experiments with Naphthylamines.

Two-tenths of a gram of dimethyl-α-naphthylamine[2] and 0.2 gram of trichlorquinone were dissolved in 1 cc. of benzene and warmed on the water-bath. As the benzene slowly evaporated, a deep blue solution was obtained, from which the addition-compound was deposited in blue-black, lustrous crystals, after standing in the cold for from 1–2 hours. The substance was decolorized by solvents. It would have been easy to analyze this and several of the substances mentioned later, but, in view of the constancy of the results already obtained, it did not seem worth while to take the time for additional analyses.

Chloranil gave a blue oil, when dimethyl-α-naphthylamine was added to its solution in benzene. This did not solidify even in a mixture of ice and calcic chloride ; it was not decolorized by the common solvents, but a few minutes on the water-bath converted it into a red oil, which gave a strong test for hydrochloric acid. Quinone gave a light red oil with dimethyl-α-naphthylamine ; trichlortoluquinone a purple color.

Diethyl-α-naphthylamine[3] was added to a benzene solution of trichlorquinone and the mixture allowed to stand 10 minutes, when, upon evaporating off the benzene with a current of air, blue needles of the addition-compound were obtained, which became sticky if allowed to stand in the solution and, after several hours, were converted into a red tar. The diethyl-α-naphthylamine gave a dark red color with quinone, with trichlortoluquinone a dark blue, with 1,4-naphthoquinone a red.

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[1] L. Clarke : THIS JOURNAL, 33, 496 (1905).

[2] Made according to Friedländer and Welmans : Ber. d. chem. Ges., 21, 3124.

[3] Prepared according to Morgan. J. Chem. Soc., 77, 823.

Diethyl-β-naphthylamine[1] was added to trichlorquinone, dissolved in ether; as the ether evaporated, the addition-compound crystallized out in sharp needles, black by reflected, greenish by transmitted light. Bromanil, under similar conditions, gave black, lustrous prisms. Quinone gave a light purple color. Trichlortoluquinone, dissolved in benzene, was mixed with the amine and if, after warming for a few minutes on the water-bath, the benzene was allowed to evaporate, the product was a green oil, which deposited long, slender, blue-black needles, after it had stood a few minutes.

α-Naphthylamine mixed with a toluene solution of trichlorquinone, gave a bluish-green color, but no crystals could be obtained, as a brown wax was formed in about 10 minutes. With monochlorquinone, in toluene solution, a purple color was obtained, which soon turned brown; with quinone brownish-red needles, which seemed comparatively stable; with trichlortoluquinone deep blue crystals, also comparatively stable.

Experiments with Other Amines.

Diphenylamine gave, with either chloranil or trichlorquinone, black, very unstable crystals; with bromanil a deep blue color.

Pyridine gave a red color at once with chloranil and, after standing 10 minutes, brownish-red plates separated, which changed to a black wax in less than a minute.

Monomethylaniline gave a deep blue color with trichlorquinone or chloranil.

Tetramethyldiaminotriphenylmethane gave with quinone, in benzene solution, a violet color, and, on evaporating off the benzene slowly with a stream of air, flat prisms of a purple-violet color were obtained.

CAMBRIDGE, MASS.,
May 26, 1905.

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[1] Morgan: J. Chem. Soc., 77, 823.

Contributions from the Chemical Laboratory of Harvard College.

THE ACTION OF METHYL ALCOHOL ON HEXABROMORTHOQUINOPYROCATECHIN ETHER.

By C. Loring Jackson and P. A. Shaffer.

After Porter and one of us[1] had found that methyl alcohol forms with tetrabromorthobenzoquinone three addition-compounds—$(C_6Br_4O_2)_2.CH_3OH$ in the α- and β-isomers and $(C_6Br_4O_2)_4.CH_3OH$[2]—it became of interest to see whether other orthoquinones behaved in the same way. We have, therefore, studied the action of methyl alcohol on hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2C_6Br_2O_2$, which may be considered a tetrabromorthoquinone with 2 atoms of bromine replaced by the pyrocatechin residue, $C_6Br_4O_2$. Our experiments showed that when these bodies stood at ordinary temperatures a reaction did take place, but so slowly that even after 6 months not enough of the product had been formed for analysis and study. The presence of nitrobenzene as a solvent increased the yield, but still left much to be desired, so that we could hardly have determined the nature of this product if we had not found a method which gave it easily, with essentially a quantitative yield. This consisted in adding to the hexabrom ether, suspended in methyl alcohol, just enough sodic methylate to bring it into solution when, upon the addition of an acid, the product obtained showed itself, by its properties, identical with that made by the direct action of methyl alcohol. Its formula is $C_{12}Br_6O_4.(CH_3OH)_2$, so that it is formed by the addition of 2 molecules of methyl alcohol to 1 of the ether. It crystallizes in white, rhombic plates, which melt, with reddening, at 220°–221°. This decomposition by heat would indicate that it belongs to the α-series, but no addition-compound has been obtained from tetrabromorthoquinone with this proportion of methyl alcohol, so that, although related to the α-series, it does not strictly belong to it.

By determining the amount of sodic methylate necessary to make the compound we found that its sodium salt had this formula, $C_{12}Br_6O_4.CH_3OH.CH_3ONa$, and gave a neutral reaction with litmus. We could not find out whether it also gave another salt with twice as much sodium, as the sodium salts were so unstable that we did not obtain them in a state fit for analysis. The colored decomposition-products of the salt need further investigation.

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[1] This Journal, 31, 89 (1904).

[2] Jackson and Carlton: *Ibid.*, 34, 422 (1905).

Several other reactions of the hexabrom ether were studied in a preliminary way and yielded results which will be investigated in this laboratory.

Phenylhydrazine, diluted with nitrobenzene, reduced it to the hexabromdihydroxypyrocatechin ether,

$$C_6Br_4O_2C_6Br_2(OH)_2,$$

furnishing the most convenient method for preparing this substance yet discovered.

EXPERIMENTAL.

The hexabromorthoquinopyrocatechin ether,

$$C_6Br_4O_2C_6Br_2O_2,$$

was made by the method described by Koch and one of us,[1] in which we have introduced the following improvements: In making the tetrabrompyrocatechin, instead of recrystallizing the crude product (obtained from 20 grams of pyrocatechin) from 200 cc. of glacial acetic acid, it was washed first with about 100 cc. of this acid and then recrystallized from 75 cc. of it. The same portions of glacial acetic acid were employed repeatedly in different preparations, which led to a great economy in the amount of acid used, and increased the yield of tetrabrompyrocatechin without the trouble of working over the mother-liquors. After the crystallization the white product was washed with distilled water, which caused no darkening if, as usual, the product was pure; but if it was not, the dark impurities were precipitated from the adhering solution. The tetrabrompyrocatechin thus obtained melted between 186° and 187° and was, therefore, pure enough for our work. The yield varied from 78 to 80 per cent of the theory.

In oxidizing the tetrabrompyrocatechin to the orthoquinone, much better yields were obtained if the acetic acid solution was cooled to about 12° before adding the nitric acid and the water added, after oxidation, was also cooled to 3°–4°. We found too (as observed by Carlton) that much more water should be used, the best amount for 15 grams of tetrabrompyrocatechin being 2 liters. With this cooling and dilution the quinone decomposed so slowly that no remarkable speed was necessary in filtering and washing it. It was found, however, that 15 grams was the largest amount that could be conveniently handled in this way and this gave 11–12 grams of tetrabromorthoquinone.

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[1] THIS JOURNAL, 26, 34 (1901).

The yield of the hexabromorthoquinopyrocatechin ether[1] was about 75 per cent.

Action of Methyl Alcohol on Hexabromorthoquinopyrocatechin Ether.

In these experiments the ether was treated with methyl alcohol to see if it behaved like tetrabromorthoquinone. Two grams of the ether, mixed with 5 cc. of methyl alcohol, stood in a corked flask, at ordinary temperatures, for 6 months. At the end of this time it was found that a small quantity of a new substance had been formed, which crystallized in characteristic, rhombic plates. In the hope of hastening the action, 5 grams of the ether were boiled with 50 cc. of methyl alcohol, in a flask with a return condenser, for 2 days, but the filtrate from the unattacked ether yielded, after evaporation, a small, brown residue and none of the rhombic plates of the previous experiment. A better result was obtained when 5 grams of the ether, dissolved in 25 cc. of nitrobenzene and mixed with 50 cc. of methyl alcohol, were allowed to stand in a corked flask. After several weeks the rhombic plates began to appear and continued to be deposited for some months, but even this method did not give a satisfactory yield. Fortunately, a better method of preparing this substance was discovered in the action of sodic methylate on the ether, as described in the following section.

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[1] THIS JOURNAL, **26**, 35 (1901).

Action of Sodic Methylate on Hexabromorthoquinopyrocatechin Ether.

Ten grams of the ether, suspended in 100cc. of methyl alcohol, were brought into solution by the addition of just the right quantity of a solution of sodic methylate in methyl alcohol, containing 2 per cent of sodium. Hydrochloric acid or sulphuric acid was then added drop by drop, until the liquid had become slightly acid, which was shown by its change in color. After this the mixture was diluted with 200 cc. of methyl alcohol, heated to boiling for a few minutes on the steam-bath, filtered hot from the sodium salt precipitated and the filtrate cooled by immersion in ice-water for several hours, when the rhombic plates crystallized out. These were purified by washing with hot water till free from sodium salt and recrystallizing from hot alcohol, until they showed the constant melting-point 221°, when they were dried at 100° for analysis:

I. 0.4082 gram substance gave 0.3260 gram CO_2 and 0.0397 gram H_2O.

II. 0.4691 gram substance gave 0.3874 gram CO_2 and 0.0476 gram H_2O.

III. 0.2970 gram substance gave, by the Carius method, 0.4468 gram AgBr.

IV. 0.2559 gram substance gave 0.3845 gram AgBr.

	Calculated for $C_{12}Br_6O_4.(CH_3OH)_2$.	Found.			
		I.	II.	III.	IV.
C	22.34	21.80	22.52		. .
H	1.06	1.08	1.12	. .	. .
Br	63.83	. .	. .	64.02	63.93

The substance is formed, therefore, by the addition of 2 molecules of methyl alcohol to 1 of the ether. The yield is essentially quantitative.

Properties of the Methyl Alcohol Hexabromorthoquinopyrocatechin Ether, $C_6Br_4O_2C_6Br_2O_2.(CH_3OH)_2$.—The substance crystallizes from alcohol in white, rhombic plates, which melt at 220°–221° with decomposition and evolution of gas. The compound begins to turn red at about 170°, if heated slowly. The products of this decomposition by heat are probably the original ether and methyl alcohol. It is soluble in benzene or acetone; slightly soluble in alcohol or methyl alcohol; boiling alcohol dissolves about 4.3 per cent of it; insoluble in water. Strong hydrochloric acid did not seem to act on it, even when hot. A mixture of hot glacial acetic acid and fuming nitric acid dissolves it with a slightly red color, but on dilution with water the unaltered compound seems to be precipitated. Treatment with zinc and acetic acid apparently produced no change in it even after several weeks.

The substance forms a sodium salt. In fact this salt is the immediate product of the action of sodic methylate on the hexabrom ether. Several attempts were made to prepare this salt in a state of purity, but without success. As it is soluble in water as well as methyl alcohol, we tried to obtain it by evaporation, but, if this was carried on at low temperatures *in vacuo*, the residue turned dark green as soon as it became dry, and on treating such a residue with methyl alcohol a red solution was formed and a few of the rhombic crystals of the methyl alcohol compound were left. If the methyl alcohol solution of the salt was evaporated nearly to dryness, and water added at once, complete solution followed, but if it was allowed to stand a short time it turned green and then was only partially dissolved in water, giving a red solution, as described above. On boiling this solution with the insoluble residue, rhombic crystals of the free methyl alcohol compound were formed.

Although the salt could not be obtained in a state fit for analysis, we were able to determine its composition by a titration experiment. For this purpose a solution of sodic methylate in methyl alcohol was used, which contained 0.00416 gram of sodium in each cubic centimeter. This was added, from a burette, to 0.632 gram of the ether, suspended in 25 cc. of methyl alcohol and the flask containing the mixture was well shaken after each addition, when it was found that 5.1 cc. of the sodic methylate solution were needed to bring the ether into solution. These contain 0.0212 gram of sodium, whereas, if 1 atom of sodium had been used for each molecule of the ether, the amount would be 0.0211 gram. The solution thus obtained was neutral to litmus and became alkaline on the addition of more of the sodic methylate solution. It is evident, from this experiment, that our new substance forms a salt,

$$C_{12}Br_6O_4.CH_3OH.CH_3ONa,$$

with a neutral reaction. We are unable to determine whether it also forms a salt containing 2 atoms of sodium.

The amount of bromine removed from the ether by sodic methylate did not rise above a mere trace, as 0.2 gram of the ether, mixed with methyl alcohol and sodic methylate, and then acidified with nitric acid and evaporated to dryness, gave, in the filtered solution of the residue, only a very slight turbidity with argentic nitrate.

Our work on the green decomposition-product of the salt was left unfinished from want of time, but some account of it may be given. If a neutral solution of the salt, formed by adding sodic methylate to the ether in the proportion of 1 molecule of each, was evaporated and the residue, after some time, dissolved in water, the red solution was found to have become acid to litmus paper, which we think was due to the liberation of a little of the methyl alcohol compound, $C_{12}Br_6O_4.(CH_3OH)_2$. The red color of this solution was due to a substance which was obtained in small amounts when the ether was treated with a large excess of sodic methylate, in methyl alcohol solution, and the product allowed to evaporate and stand over night. Upon adding very little water to the residue the new substance was left undissolved, in red needles. The following method gave what seemed to be the same product with a better yield :

The methyl alcohol compound, $C_{12}Br_6O_4.(CH_3OH)_2$, was boiled with a 20 per cent solution of sodic hydrate, when, on cooling, red needles appeared. The mixture was allowed to stand over night and then the crystals were filtered out on the pump and purified by crystallization from water, or better, as the substance was rather too soluble in water, a saturated aqueous solution of the product was treated with one-third to one-quarter of its volume of strong sulphuric acid, which precipitated the substance in light red needles. These, on recrystallization from water, took on the darker red color of the preparations purified by crystallization alone. Unfortunately, in the time at our disposal, we could not prepare enough of this substance for analysis. It crystallizes in red needles, which do not melt, but at about 280° decompose with evolution of gas, leaving a black, charred mass. This decomposition-point seems to be nearly as well defined as a melting-point. The substance is soluble in both water and alcohol.

When the methyl alcohol compound was treated with methyl alcohol and bromine, a new substance was formed which melted, in the crude state, at about 150° without decomposition. This seemed to be different from the white product[1] of the action of bromine and methyl alcohol on the red hexabrom ether, as a sample of that melted at about 212°, with reddening and evolution of gas. What seemed to be still a third product was made by adding a little bromine to acetone and then treating the methyl alcohol compound with the colorless liquid.

Other Reactions of the Hexabromorthoquinopyrocatechin Ether.

Sodic ethylate, in ethyl alcohol solution, acted very slowly on the ether and gave a dark-colored product different from the methyl alcohol compound, but resembling in appearance that obtained by heating the ether with aqueous sodic hydrate. This last reagent had no perceptible action in the cold.

Bromine in ethyl alcohol, on the other hand, gave a white product after standing for several weeks with the red ether. No action was observed with benzyl alcohol or glacial acetic acid, even after standing for 7 months. Phenol gradually dissolved it, but on removing the phenol with water the unaltered ether was recovered.

Phenylhydrazine acted vigorously with the solid ether, forming a dark brown product, with evolution of white fumes. When the reaction was rendered less violent by the use of a solvent, a much purer product was obtained; we, therefore, found it best to proceed as follows: One part, by weight, of the ether was mixed with 5 parts of nitrobenzene and then phenylhydrazine was added, drop by drop, shaking thoroughly after each addition, until the red color of the ether had been discharged. The nitrobenzene was then washed out with alcohol and the light brown residue was purified by recrystallization from boiling alcohol, when it appeared in long, white needles which mat together like asbestos. On standing for some days, in the light, the crystals turn brown. They show the solubilities of the hexabromdihydroxypyrocatechin ether, $C_6Br_4O_2C_6Br_2(OH)_2$, and it was proved to be this substance by a careful comparison of our product with one obtained by Dr. Russe in his work on the action of acetone on tetrabromorthoquinone. This reaction with phenylhydrazine is the easiest method yet found for preparing the hexabromdihydroxypyrocatechin ether.

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[1] This substance was made by Porter.

The work on the substances mentioned in this paper will be continued in this laboratory.

CAMBRIDGE, MASS.,
June 12, 1905.

THE ATOMIC WEIGHT OF RADIUM AND THE PERIODIC SYSTEM.

BY HARRY C. JONES.

The question of the atomic weight of radium cannot be regarded, as yet, as settled. We have, on the one hand, the determination, by purely chemical means, made by Mme. Curie,[1] which gave the value 225. On the other, we have the work of Runge and Precht,[2] based on a physical method, which gave a much higher value—258.

It is difficult, at present, to decide between these two. The value based upon spectrum analysis (258) places radium in the periodic system *after* thorium and uranium. In terms of the relation between the mass of the atom and its radio-activity, this is the position which it should occupy. The greater the mass of the atom, the less its stability and, consequently, the greater its radio-activity.

Various lines of argument have been advanced in favor of the value 225. Perhaps the most important of these is the argument based upon the position of radium in the periodic system. Radium is closely allied chemically to barium, and the value 225 for its atomic weight places it in the same *group* with barium, in *series twelve.*

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[1] Ann. Chim. Phys. [7], **30**, 137 (1904).

[2] Phil. Mag. [6], **5**, 476 (1903).

This line of argument has had considerable weight, and has been used in favor of the smaller mass for the atom of radium.

The object of this paper is to point out that if the atomic weight of radium is slightly greater than 250, it would find a place in the periodic system quite in accord with all its chemical and physical properties. Indeed, the position which it would then occupy would be rather more satisfactory than that which it would take if its atomic weight were 225.

If the atomic weight of radium were 252 to 256 it would fall in Group II. of the periodic system, along with barium and its homologues, but in a new series—*series thirteen.*

That this is the case can be seen by a glance at Mendeléeff's table of the periodic system. If we compare the atomic weights of the elements in a given group and in any two succeeding series, we shall find for the elements with the higher atomic weights a difference in the atomic weights, in general, of from 25 to about 31 or 32 units.

Thus, the atomic weight of strontium is 87.6, that of cadmium 112.4—difference 24.8. The atomic weight of barium is 137.4, which differs from that of cadmium by 25 units.

Passing to Group III., the atomic weight of yttrium = 89, differs from that of indium = 115 by 26 units. Indium differs from lanthanum = 138.9 by 23.9 units, lanthanum differs from ytterbium = 173 by 34.1, and ytterbium differs from thallium = 204.1 by 31.1 units.

Turning to Group IV. similar relations manifest themselves. Zirconium, atomic weight 90.6, differs from tin, whose atomic weight is 119.0, by 28.4 units. Tin differs from cerium, whose atomic weight is 140.25, by 21.25 units. Cerium differs from lead, whose atomic weight is 206.9, by 66.65, but since cerium is in Series 9 and lead is in Series 11, and there is no member in this group in Series 10, we must divide the above difference by 2, which gives us a difference per series of 33.32. Lead differs from thorium, whose atomic weight is 232.5, by 25.6 units.

In Group V. the following differences appear: Vanadium, with an atomic weight of 51.2, differs from arsenic, with an atomic weight of 75, by 23.8. Arsenic differs from niobium = 94, by 19 units. Niobium from antimony = 120.2 by 26.2 points. Antimony from tantalum = 183 by 62.8, but since one series is missing between these two, this difference must be halved = 31.4. Tantalum differs from bismuth = 208.5 by 25.5.

In Group VI. relations of the same kind appear. Chromium, whose atomic weight is 52.1, differs from selenium = 79.2 by 27.1 units. Selenium differs from molybdenum = 96 by 16.8 units. Molybdenum differs from tellurium = 127.6 by 31.6 points. Tellurium differs from tungsten = 184.0 by 56.4, but as one series is here missing this must be halved = 28.2. Tungsten differs from uranium = 238.5 by 54.5, and halving this, on account of the missing series, we have 27.2.

The above relations suffice to show that two successive members in any group of the periodic system usually differ, in their atomic weights, by a number that is close to from 25 to 28 and may reach 31 or 32, or even higher. This shows that an atomic weight slightly greater than 255, and which might be as high as 257 or 258, would place radium quite as satisfactorily in the periodic system as the lower value 225.

It might be objected that there is no other member of Series 13 known, and that it would be *creating a new series* just for one element—radium.

It is difficult to see the force of this argument in the light of the facts. In the first place, we know, at present, only two members of Series 12—thorium and uranium. Both of these are radioactive, but only feebly so.

While the placing of radium in Group II., Series 12, brings it in the same group with its chemical relative barium, it at the same time places it in a position which is not in keeping with its most characteristic physical properties. Think of radium as compared with thorium and uranium, or with any other chemical element. It is at least 1,500,000 times as radioactive as uranium. It has the property of charging itself electrically, of lighting itself, and of giving off enormous quantities of heat energy. It is the only element known that has any of these properties to a determinable degree.

Further, it is very unstable, breaking down spontaneously and yielding another chemical element—helium—as one of its decomposition-products.

When we think of these properties alone it seems much more natural to place radium in a series by itself, following the series containing the slightly radioactive elements—thorium and uranium—than to place it in a series with any other chemical element or elements.

If we examine the evidence existing in favor of the value 225 we find, in the first place, the direct determination by Mme. Curie. It must be admitted that this is far from satisfactory, for a number of reasons. The small quantity of material at disposal made the result less accurate, assuming that the material was pure. A number of the operations to which it was subjected, such as removal of the water by heating in the air, are open to criticism.

Another argument in favor of the 225 value is based upon the fact, now pretty clearly established, that radium is a decomposition-product of uranium and must have a smaller atomic mass than the substance which produced it. This line of argument has been invalidated by the observation that *radium is certainly not formed directly from uranium*, but intermediate substances are produced and, as Joly[1] has pointed out, the radium probably results from the interaction of these products with some of the elements in pitchblende. Its atom could then easily have a mass greater than the atom of uranium itself, since radium would thus be a product of synthesis and not of decomposition. It must be stated that certain determinations by Watts[2] and others, using relations between the spectral lines, led also to a value close to 225. The meaning of this remains to be explained.

The direct argument in favor of the higher value is furnished by the beautiful investigation of Runge and Precht.[1] By means of certain relations between the spectral lines and the atomic weights of the elements producing them, which have been shown to hold for the members of a given group, as the magnesium, calcium, strontium, barium group, they were led to an atomic weight for radium of 257.8, or in round numbers 258.

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[1] Nature, **70**, 80 (1904).

[2] Phil. Mag., [6], **6**, July (1903).

As shown above, this would not move radium "two rows further down in the column Mg, Ca, Sr, Ba," as stated by Runge and Precht, and to which objections must be offered, but *only one row*, making it the only member of Series 13.

The atomic weight of radium can be settled, finally, only after a considerable amount of pure material is available. As some time must elapse before this is realized, the best we can do, at present, is to take the evidence available. The object of the present note, as has been stated, is to call attention to the fact that the argument based upon the periodic system, in favor of 225 as the atomic weight of radium, is not well founded. Indeed, the evidence from the periodic system is certainly as strong, and in the opinion of the writer much stronger, in favor of a higher value, which would be very nearly that found by Runge and Precht.

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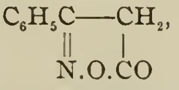
PHENYLISOXAZOLONE.

BY ALFRED TINGLE.

In a recent article[2] Posner describes the preparation of phenylisoxazolone,  $\begin{array}{l}C_6H_5C{-\!\!-}CH_2,\\ \quad\;\| \qquad\; | \\ \quad\; N.O.CO\end{array}$ from β-oxamino-β-phenylpropionic acid, $C_6H_5CH(NHOH)CH_2COOH$, previously[3] mistaken by him for α-oxamino-β-phenylpropionic acid,

$$C_6H_5CH_2CH(NHOH)COOH.$$

It seems desirable to call attention to the fact, which he appears to have overlooked, that the above phenylisoxazolone was first prepared by Claisen and Zedel,[1] by the action of hydroxylamine on ethyl benzoylacetate and by me, subsequently, from hydroxylamine and ethyl cinnamate, in the course of an investigation on "The Reactions of Aniline and Hydroxylamine with Hydroxy- and Unsaturated Compounds."[2] This work has had to be suspended on account of my removal from the United States. A knowledge of it would have saved Posner some labor and probably would have prevented his making the error into which he has fallen. I hope to resume my study of this subject later.

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[1] *Loc. cit.*

[2] Ber. d. chem. Ges., **38**, 2316 (1905).

[3] *Ibid.*, **36**, 4305 (1903).

IMPERIAL PROVINCIAL COLLEGE,
CHINANFU, SHANTUNG, CHINA.
Sept. 10, 1905.

REVIEWS.

FOOD PRESERVATIVES, THEIR ADVANTAGES AND PROPER USE. The Practical versus the Theoretical Side of the Food Problem. By R. G. ECCLES, M.D., Pharm.D. With an Introduction by E. W. DUCKWALL, M.S. New York: D. Van Nostrand Company. 1905. pp. 202. Price, 50 Cents.

It is difficult to believe in the competency and sincerity of the writer of this book and therefore impossible to criticize it without writing a new volume. No examples need be given to justify the above opinion, as it is borne out on every page. The entire book is a tangled mixture of facts, misstatements and theories, which can hardly fail to mislead those unfamiliar with the subject. It is worthy of no further notice than is required to condemn it unreservedly. There is, of course, much to be said in favor of the judicious use of food preservatives and, when discreetly employed, they are undoubtedly a safeguard. Legislation controlling their use is, however, indispensable to prevent the more unscrupulous manufacturers from doing great harm. A. S. L.

AN INTRODUCTION TO CHEMICAL ANALYSIS FOR STUDENTS OF MEDICINE, PHARMACY AND DENTISTRY. By ELBERT W. ROCKWOOD, M.D., PH.D., Professor of Chemistry at the University of Iowa. Second revised edition. Philadelphia: P. Blakiston Son's & Co. 1904. Price, $1.50 net.

A review of the first edition of this useful manual appeared in 1902.[3] The publication of a second edition shows that it has gained the approval of instructors. E. R.

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[1] Ber. d. chem. Ges., **24**, 140.

[2] THIS JOURNAL, **24**, 50 (1900).

[3] *Ibid.*, **27**, 235.

THE DETECTION OF POISONS AND STRONG DRUGS, Including the Quantitative Estimation of Medicinal Principles in Certain Crude Materials. By DR. WILHELM AUTENRIETH, Professor in the University of Freiberg. Authorized translation from the third German edition by WILLIAM H. WARREN, PH.D., Professor of Chemistry, Medical Department of Washington University, St. Louis, Mo. Philadelphia: P. Blakiston's Sons & Co. 1905. Price, $1.50 net.

A translation of Professor Autenrieth's well-known manual is welcome and will prove very helpful to English-speaking students of chemistry, of medicine and of pharmacy. Professor Warren's translation is clear and well-worded.

Autenrieth's system is to classify poisons in four groups. Group I. comprises those volatile substances which may be distilled with steam, from an acid solution, without decomposition and includes yellow phosphorus, prussic and carbolic acids, chloroform, iodoform, aniline, nitrobenzene and carbon bisulphide. Group II. consists of non-volatile organic substances which do not distil with steam from acid solution, but may be extracted from impure mixtures by hot alcohol in the presence of tartaric acid; this group includes the alkaloids and many drugs, acetanilide, phenacetine, antipyrine, sulphonal, etc. Group III. includes the poisonous metals. In Group IV. we find acids, alkalies and a few poisons which do not fit into the preceding groups. Within the groups the individual poisons are detected by special reactions, chosen with excellent judgment.

The translator says in the introduction, "the brief comments of the author upon the fate, distribution and elimination of poisons in the animal body are a valuable feature of the last edition. The student learns what organs of the body should be examined for a poison in an actual analysis, what alterations it undergoes in metabolism and how it is eliminated. The introduction of the biological methods used in detecting arsenic and human blood add much to the completeness of the book." Frequent references to the literature of the subject increase the value of the work. E. R.

MANUAL OF CHEMICAL ANALYSIS, as Applied to the Assay of Fuels, Ores, Metals, Alloys, Salts and Other Mineral Products. By EUGENE PROST, D.SC., of the University of Liège. Translated by J. CRUICKSHANK, B.SC., F.C.S. London: Maclaren & Sons; New York: D. Van Nostrand Co. 1904. Price, $4.50 net.

This is a comprehensive but condensed manual; it is clear, the analytical methods are well chosen and it is a convenient work for the student.

The publishers could easily have printed it on thin, good paper, with decent type and have sold it at half the price demanded. The paper used is thick and coarse, the type worn and blurred, the drawings rude, the price ($4.50 net) out of proportion to the number of pages (300).

It is impossible to recommend this edition to students, they will do better to buy Rhead and Sexton's admirable manual,[1] which covers the same ground, but more completely, and is excellently printed and illustrated. E. R.

EINLEITUNG IN DIE CHEMISCHE ANALYSE. Erstes Heft. Kurze Anleitung zur Qualitativen Analyse, zum Gebrauche beim Unterricht in Chemischen Laboratorien. Bearbeitet von DR. LUDWIG MEDICUS, Professor an der Universität Würzburg. Zwölfte und dreizehte verbesserte und vermehrte Auflage. Tübingen: H. Laupp. 1905. Price, M. 2.

A review of the eleventh edition of Professor Medicus' valuable manual appeared in a former number.[2]

In this new edition one or two minor additions have been made, but, in the main, the book is unchanged. The dissociation theory is explained in the introduction, but is not utilized in the text. This book, it should be remembered, is the most popular manual in use in German laboratories and indicates a conservative spirit in Germany in the teaching of qualitative analysis. E. R.

A SHORT INTRODUCTION TO THE THEORY OF ELECTROLYTIC DISSOCIATION. By J. C. GREGORY, B.Sc. (Lond.), A.I.C. London, New York and Bombay: Longmans, Green & Co. 1905. pp. 76. Price, 50 cents.

This little booklet is just about what might reasonably be expected from the title. Even a casual glance brings out some peculiar English. On page 10 we read, "The digestion and incorporation within the general scientific system of new and apparently abnormal facts, must first be attempted by temporary attempts at explanation." On page 21, "Conductivity and resistance are reciprocals, and the less the latter is, the greater is the former."

On page 35, "It is evident that the more soluble a precipitate is, the greater does its solubility-product tend to be."

The reasons given on page 11, for assuming that molecules in solution are broken down into ions, are so inadequate as to leave an entirely wrong impression.

The book may prove helpful to those who cannot go more fully into the subject. H. C. J.

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[1] Rhead and Sexton. "Assaying and Metallurgical Analysis." Longmans, Green & Co. 1902 (431 pages). Reviewed in this JOURNAL, **30**, 82 (1903).

[2] THIS JOURNAL, **27**, 235.

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AMERICAN

CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Harvard College.

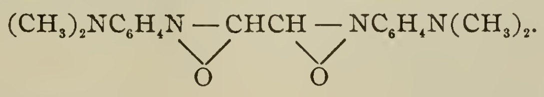
THE ACTION OF ETHYLENEDIBROMIDE ON PARA-NITROSODIALKYLANILINES. II.

BY HENRY A. TORREY.

In an earlier paper on this subject[1] it was shown that when *p*-nitrosodimethylaniline and ethylene dibromide were heated together at a temperature of 80°–90°, the following reaction occurred :

$$4C_6H_4(NO)N(CH_3)_2 + C_2H_4Br_2 = [C_6H_4(NO)N(CH_3)_2]_2C_2H_2 + 2C_6H_4(NO)N(CH_3)_2HBr.$$

That is, the hydrobromide of nitrosodimethylaniline and a base, formed from the union of 2 molecules of dimethylaniline and the acetylene group, were produced. One of the structural formulas then suggested for this base was



$$(CH_3)_2NC_6H_4\underbrace{N-CH}_{O}\underbrace{CH-N}_{O}C_6H_4N(CH_3)_2.$$

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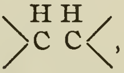
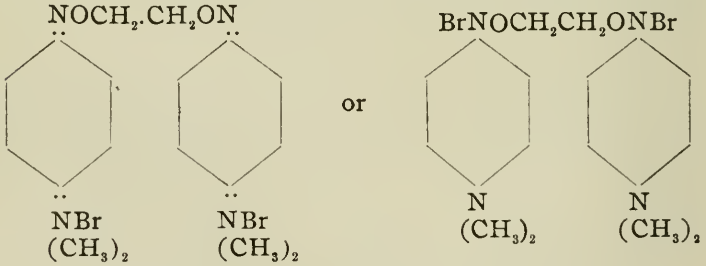
[1] THIS JOURNAL, 28, 107.

That this is actually its constitution is now proved, since it is found to be identical with the tetramethyldiaminoglyoxim-N-phenyl ether obtained by H. v. Pechmann and W. Schmitz by the action of diazomethane on *p*-nitrosodimethylaniline.[1] It was shown by these authors that the formation of glyoxim-N-phenyl ethers was a general reaction for diazomethane on aromatic nitroso compounds.[2]

In this reaction of ethylene dibromide some intermediate compound is very likely formed before the glyoxim-N-phenyl ether is produced, since the latter compound consists of 2 molecules of *p*-nitrosodimethylaniline united by



but acetylene itself does not act on *p*-nitrosodimethylaniline, whereas, with methyl iodide and benzoyl chloride it has been shown that addition-products are formed.[3] Such an intermediate body with ethylene dibromide was not isolated, but, as was suggested in a former paper, it is highly probable that an addition-product such as



is formed, which splits off hydrobromic acid with the production of the tetramethyldiaminoglyoxim-N-phenyl ether. If the reaction of ethylene dibromide on *p*-nitrosodimethylaniline is carried on in alcoholic solution, tetramethyldiaminoazoxybenzene is produced. A certain amount of this body is also formed, together with the glyoxim ether, if the temperature is allowed to rise too high when the two substances are heated together alone.

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[1] Ber. d. chem. Ges., **31**, 293.

[2] *Ibid*, **30**, 2461, 2871.

[3] *Ibid*., **26**, 1756; **30**, 933.

The melting-point given by v. Pechmann and Schmitz for the glyoxim derivative is 245°, while that given by me is 230°–240°, but decomposition occurs and the point of decomposition depends, somewhat, upon the rapidity of heating. A further proof of its identity is given by its conversion into tetramethyldiaminoglyoxaldianil, by means of dilute nitric acid, a reaction observed by v. Pechmann and Schmitz with hydrochloric acid. The glyoxim phenyl ether is very unstable toward mineral acids.

When 5 grams of this body were slowly added to 38 cc. of 15 per cent nitric acid, diluted with 38 cc. of water, a solid separated which proved to be the nitrate of *p*-nitrosodimethylaniline, as shown in a former paper.[1] When the precipitate was removed by filtration and the filtrate was made alkaline by sodium carbonate, a reddish-yellow precipitate fell, which was collected on a filter, washed with water and alcohol and dried on a clay plate. By crystallization from toluene a body was obtained in the form of yellow plates, melting at 256°–257°.

The analysis, melting-point and reaction of this compound show it to be tetramethyldiaminoglyoxaldianil,

$$(CH_3)_2NC_6H_4N : CHCH : NC_6H_4N(CH_3)_2.$$

I. 0.2003 gram substance gave 0.5391 gram CO_2 and 0.1437 gram H_2O.

II. 0.1408 gram substance gave 0.3753 gram CO_2 and 0.1016 gram H_2O.

III. 0.0902 gram substance gave 15 cc. N at 21°.3 and 765 mm.

	Calculated for $[(CH_3)_2NC_6H_4N]_2C_2H_2$.	Found.		
		I.	II.	III.
C	73.47	73.41	72.70	. .
H	7.48	7.97	8.02	. .
N	19.04	. .	. .	19.26

Properties of Tetramethyldiaminoglyoxaldianil.—As would be expected, reduction of this body by zinc and sulphuric acid gives *p*-aminodimethylaniline, which was isolated by adding an excess of sodic hydrate and shaking out with ether. The ethereal solution, dried with solid potassic hydrate, gave, after distilling off the ether and evaporating in a dry vacuum, colorless crystals which, on crystallization from ligroin, melted at 37°–39° (m. p. *p*-aminodimethylaniline 41°). These crystals gave a strong methylene blue reaction.

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[1] This Journal, 28, 107.

That the glyoxalanil is itself somewhat hydrolyzed by dilute acids is evident from the fact that such solutions give the methylene blue reaction.

The weakness of the union at the double bonds is still further illustrated by the products obtained by the action of salicylic aldehyde and benzoyl chloride.

Action of Salicylic Aldehyde on Tetramethyldiaminoglyoxaldianil.

When the dianil is boiled with an alcoholic solution of salicylic aldehyde it is converted, almost quantitatively, into *o*-oxybenzylidene-*p*-aminodimethylphenylamine :

$$(CH_3)_2NC_6H_4N : CHCH : NC_6H_4N(CH_3)_2 + 2HOC_6H_4CHO = \\ 2(CH_3)_2NC_6H_4N : CHC_6H_4OH + OCHCHO.$$

Five grams of the dianil were boiled for 40 minutes with 1 gram of salicylic aldehyde, dissolved in 45 cc. of alcohol. From this, filtered hot, there separated, on cooling, beautiful orange plates which melted at 134°–135°. The melting-point was not raised by recrystallization.

The melting-point, the analytical results which are given below and a comparison with a sample of *o*-oxybenzylidene-*p*-aminodimethylphenylamine, made directly from *p*-aminodimethylaniline and salicylic aldehyde,[1] leave no doubt as to its identity. Analysis :

I. 0.2480 gram substance gave 0.6791 gram CO_2 and 0.1520 gram H_2O.

II. 0.1701 gram substance gave 18.35 cc. N at 26°.5 and 764 mm.

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[1] Ber. d. chem. Ges., **18**, 593.

	Calculated for $(CH_3)_2NCH_4N : CHC_6H_4OH$.	Found. I.	II.
C	75.00	74.66	. .
H	6.66	6.81	. .
N	11.66	. .	12.01

Action of Benzoyl Chloride on Tetramethyldiaminoglyoxaldianil.—By repeated treatment of the dianil with benzoyl chloride and dilute sodic hydrate, a cleavage of the molecules occurs and benzoyl *p*-aminodimethylaniline is formed.

When the benzoyl chloride is first added the dianil is taken up by the acid chloride, with formation of a dark-green mixture. After repeated treatment and frequent stirring, a light-colored product was obtained. The aqueous, alkaline solution was poured off, the residue was treated with alcohol, collected on a filter, dried on a clay plate and crystallized from boiling benzene, it separated in the form of silk-like needles. The product melted at 223°–224° and recrystallization failed to raise the melting-point. This is somewhat lower than that given by Börnstein (228°), who prepared the compound by the direct action of benzoyl chloride on *p*-aminodimethylaniline. The analytical results are those required for monobenzoyl *p*-aminodimethylaniline.[1]

I. 0.1485 gram substance gave 0.4040 gram CO_2 and 0.0911 gram H_2O.

II. 0.1449 gram substance gave 15.6 cc. N at 24° and 758 mm.

	Calculated for $(CH_3)_2NC_6H_4NHCOC_6H_5$.	Found. I.	II.
C	75.00	74.20	. .
H	6.66	6.82	. .
N	11.66	. .	12.05

Although tetramethyldiaminoglyoxaldianil is hydrolyzed by mineral acids, it gives a bronze-colored salt when chloroform solutions of the dianil and picric acid are mixed. With alcoholic mercuric chloride it gives a blue precipitate. It also gives a blue color with extremely dilute chloroform or benzene solutions of bromine, chlorine, hydrochloric acid and acid chlorides.

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[1] Ber. d. chem. Ges,, **29**, 1482.

Chloroform, when perfectly pure, dissolves it with a yellow color, but when this solvent has begun to decompose even very slightly, the color produced is green or blue.

Action of Ethylene Dibromide on p-Nitrosodiethylaniline.[1]

Tetraethyldiaminoglyoxim-N-phenyl Ether.—When *p*-nitrosodiethylaniline and ethylene dibromide were heated together on the steam-bath the reaction became so violent that it was uncontrollable, but it proceeded smoothly enough if the two substances, in the proportions of 1 part of the base to 4 parts of the ethylene dibromide, were allowed to stand at the ordinary temperature for a day or two. After the interval, a dark-colored solid separated, which was collected on a filter and dried on a porous plate. The products of this reaction are tetraethyldiaminoglyoxim-N-phenyl ether and the hydrobromide of *p*-nitrosodiethylaniline, which were isolated in the following manner: The hydrobromide was decomposed and dissolved out from the glyoxim derivative by treatment with alcohol and dilute sodic hydrate. After thoroughly washing with alcohol and drying, the product was crystallized several times from amyl alcohol. Addition of absolute ethyl alcohol to the amyl alcohol solution aided in the crystallization. The body decomposed at about 207°, the temperature depending somewhat on the rapidity of heating. That this body is identical with the tetraethyldiaminoglyoxim-N-phenyl ether obtained by v. Pechmann and Schmitz by the action of diazomethane is shown by its melting-point, its properties and the analytical results given below:

I. 0.1196 gram substance gave 0.2996 gram CO_2 and 0.0840 gram H_2O.

II. 0.1518 gram substance gave 0.3814 gram CO_2 and 0.1108 gram H_2O.

III. 0.2266 gram substance gave 27.2 cc. moist N at 22° and 764 mm.

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[1] This reaction was studied some time ago with Mr. A. L. Kelley at the University of Vermont.

	Calculated for $[(C_2H_5)_2NC_6H_4N]_2C_2H_2O_2$.	Found. I.	II.	III.
C	69.11	68.32	68.52	. .
H	7.85	7.80	8.11	. .
N	14.66	. .	. .	14.67

I wish to express to Mr. W. W. Farnum my indebtedness to him for his assistance in certain portions of this work.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN SALTS IN MIXTURES OF ACETONE WITH METHYL ALCOHOL, WITH ETHYL ALCOHOL AND WATER.

By Harry C. Jones and Eugene C. Bingham.

PART I.

HISTORICAL REVIEW.

(*a*) *Conductivity and Viscosity.*—That viscosity and conductivity are related is by no means a new idea. As early as 1856, G. Wiedemann[1] studied aqueous solutions of copper sulphate and concluded that the conductivity of a solution is directly proportional to the concentration and inversely proportional to the viscosity. When formulated this would be:

$$\frac{K\eta}{p} = \text{constant},$$

where K is the conductivity of the solution of concentration, p and η the viscosity.

Grotrian,[2] in 1876, measured the conductivity and viscosity of solutions at different temperatures, but obtained indecisive results.

Stephan,[3] in 1883, tried a third possibility, by using mixtures of alcohol and water as a solvent. He found the temperature coefficients of conductivity and of fluidity (the reciprocal of viscosity) very much alike. He observed a minimum in his curves and proposed the formula:

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[1] Pogg. Ann., **99**, 229 (1856).

[2] *Ibid.*, **157**, 130 (1876).

[3] Wied. Ann., **17**, 673 (1883).

$$\frac{\mathrm{KH}}{k\eta} = \text{constant},$$

to hold up to the minimum point, and

$$\frac{w\mathrm{KH}}{w'k\eta} = \text{constant}$$

to hold from that point on; where K is the conductivity of the equivalent aqueous solution, k the conductivity of the mixture and H and η, the corresponding viscosities. w and w' are the per cents of water in the given aqueous mixture and in the aqueous alcoholic mixture of minimal fluidity, respectively. He believed that each ion carries with it neighboring molecules of the solvent, and that ionic friction results from the friction between these and the rest of the solvent.

Dutoit and Friderich[1] introduced the association factor and concluded that, "The values of μ_v for a given electrolyte dissolved in different solvents, are a direct function of the degree of polymerization of the solvent and an indirect function of the coefficient of viscosity of these solvents."

A fourth method of changing the fluidity was resorted to by Röntgen,[2] and later by Warburg and Sach,[3] and more exhaustively by Cohen.[4] They subjected the aqueous solution to high pressure. Cohen found that, at low temperatures, the viscosity is decreased by the pressure, but that above 40° the viscosity increases with the pressure. In concentrated solutions of sodium and ammonium chlorides the viscosity increases nearly proportionally to the pressure and nearly independently of the temperature. Hauser[5] showed that, at 32°, the pressure ceased to affect the fluidity of water.

Grossman,[6] in 1883, recalculated Grotrian's results and found that the conductivity multiplied by the viscosity gave a constant independent of the temperature, and that the temperature coefficients were the same to within 1 per cent.

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[1] Bull. Soc. Chim., [3], **19**, 321 (1898).

[2] Wied. Ann., **22**, 510 (1884).

[3] *Ibid*,, **22**, 514 (1884).

[4] *Ibid.*, **45**, 666 (1892).

[5] Ann. d. Physik., **5**, 597 (1901).

[6] Wied. Ann., **18**, 119 (1883).

Arrhenius[1] worked with aqueous solutions, to which small amounts of non-electrolytes, such as acetone and methyl and ethyl alcohols, had been added. He pointed out an empirical relation between the conductivity and the fluidity, but he saw that these quantities are not simply dependent on each other, because the conductivities of dilute solutions of different salts are not the same. This empirical relation was further developed by Euler.[2]

We need only mention the work of Stringberg[3] and of Holland.[4]

Völlmer[5] investigated solutions of various salts in methyl and ethyl alcohols. He found the temperature coefficients of conductivity and fluidity to be very nearly identical.

Kohlrausch and Deguisne[6] used a formula,

$$K_t = K_{18}[1 + \alpha\,(t - 18^\circ) + \beta(t - 18^\circ)^2],$$

to represent the influence of temperature on conductivity, starting from 18° as a mean temperature. Kohlrausch[7] noted that on extrapolating this curve, aqueous solutions would reach a zero value of conductivity at about —39°, which is about the temperature where the fluidity would become zero. Bousfield and Lowry[8] showed that the viscosity of water may be represented accurately by a formula similar to the above,

$$\eta_{18} = \eta_t\,[1 + \alpha(t - 18) + \beta(t - 18)^2].$$

They found that the constants α and β are the same in the two formulas, to within the limits of experimental error. They believe, however, that these formulas will not hold at low temperatures and that the zero values cannot be experimentally realized. This belief is borne out by the work of Kunz.[9]

In an exceedingly interesting paper, Kohlrausch[10] proposes the view that "About every ion there moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion. . . . . The electrolytic resistance is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness. . . . . For a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of water, provided the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere becomes, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to observations now at hand, this would seem to be the case for the slowest moving univalent ion, Li.''

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[1] Z. physik. Chem., **9**, 487; *Ibid.*, **1**, 285 (1887).

[2] *Ibid.*, **35**, 536 (1898).

[3] *Ibid.*, **14**, 221 (1894).

[4] Wied. Ann., **50**, 261 (1892).

[5] *Ibid.*, **52**, 328 (1894).

[6] Dissertation, Strassburg, 1893.

[7] Sitz. Berlin., (1901), 1028.

[8] P. Roy. Soc., **71**, 42 (1902).

[9] Compt. rend., **135**, 788 (1902).

[10] P. Roy. Soc., **71**, 338 (1903).

Bousfield and Lowry[1] have gone farther and have shown that we should also expect to find an upper limit of conductivity, on account of the decrease in dissociation with rise in temperature. A maximum conductivity of this sort has been observed by Franklin and Kraus[2] in liquid ammonia. Potassium iodide gives a maximum in conductivity, in methyl alcohol, at 160°.[3] Noyes[4] observed a maximum conductivity with 0.1 N potassium and sodium chlorides, in water, at 280°. The formula of Slotte[5] for variation of fluidity,

$$\eta_0/\eta = (1 + bt)^n,$$

holds at low temperatures, so that combining this formula with that of Abegg and Seitz for decrease in dielectric constant,

$$D/D' = e^{-at},$$

Bousfield and Lowry[6] give, as the complete formula representing the effect of temperature on conductivity,

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[1] *Loc. cit.*

[2] This Journal, **24**, 83 (1900).

[3] Physic. Rev., **18**, 40 (1904).

[4] Z. physik. Chem., **46**, 323 (1903). J. Am. Chem. Soc., **26**, 134 (1903).

[5] Beibl., **16**, 182 (1892).

[6] P. Roy. Soc., **74**, 280 (1904).

$$\frac{K_t}{K_0} = \frac{\rho_v}{\rho_0}(1 + bt)^n e^{-at}.$$

Reference should also be made to the work of Hechler.[1]

(*b*) *Viscosity.*—The majority of workers have confined themselves either to viscosity determinations alone, or to conductivity determinations alone. We must, therefore, consider some of these if we wish to see clearly the relations between the phenomena.

We need simply mention here the work of Poiseuille,[2] Noack,[3] Pagliani and Battelli,[4] Slotte,[5] Gartenmeister[6] and Traube.[7] The monumental work of Thorpe and Rodger[8] requires more attention. They worked with very great accuracy both with pure liquids[7] and with mixtures,[9] and over a considerable range of temperature. They have shown that the formula of Slotte gives the best results. They proved, conclusively, what had been hinted at before, that "Viscosity may be taken as the sum of the attractive forces in play between the molecules; . . . . that an increment of CH_2 in chemical composition, or the substitution of an atom of Cl, Br, or I for an atom of hydrogen, brings about a definite change in the magnitude of the viscosity. It is, therefore, made evident that viscosity or intermolecular attraction is, in reality, a property of the atoms of which the molecules are composed. Isomers have nearly, but not the same viscosity, yet the effect of CH_2 is the same as in the normal compounds. The effects due to ring grouping, iso- and double-linkages, and changes in the condition of the oxygen may be quantitatively allowed for. . . . . But water and the alcohols show no agreement with the calculated values."

Hydrogen is calculated to have an effect on molecular viscosity of 44.5, carbon of 31 and iso-linkage, for example, of

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[1] Dissertation, Münster (1904).

[2] Mem. Inst. Paris, **9**, 433 (1896).

[3] Wied. Ann., **27**, 289 (1886).

[4] Atti. di R. Ac. delle Sc. d. Torino, **20**, 607 (1885).

[5] *Loc. cit.*

[6] Z. physik. Chem., **6**, 524 (1890).

[7] Ber. d. chem. Ges., **19**, 871 (1886).

[8] Phil. Trans., **185A**, 307 (1894).

[9] J. Chem. Soc., **51**, 360 (1897).

—21. The effect is shown in the following table, giving the "molecular viscosity at slope 0.0000323."

Table I.

	Normal compound.		Iso-compound.	
	Found.	Calculated.	Found.	Calculated.
Pentane	687	689	663	668
Hexane	818	809	799	788
Heptane	931	929	908	908
Octane	1035	1049		

They found both maxima and minima when working with mixtures and, in the particular case of chloroform and ether, they found a point of inflection. They believe that the maximum value is caused by a "feeble chemical combination or molecular aggregation, which is destroyed by heat or dilution."

It is to be expected that water and the alcohols would give abnormal results, since Ramsay and Shields[1] have shown that these liquids are associated. They are also abnormal in possessing a high dielectric constant.[2] Some of the characteristic properties of water, methyl alcohol, ethyl alcohol and acetone are grouped together below :

Table II.

	Mol. vol.	Viscosity.	Association.	Dielectric constant.
Water	18.0 at 0°	0.01778 at 0°	1.707 at 0°	79.46 at 0°
	18.1 at 25°	0.00891 at 25°	1.644 at 20°	73.92 at 20°
Methyl alcohol	39.5 at 0°	0.0080846 at 0°	2.65 at -90°	34.05
	40.3 at 20°	0.005530 at 25°	2.32 at 20°	
Ethyl alcohol	57.1 at 0°	0.017761 at 0°	2.03 at -90°	25.02
	58.3 at 20°	0.0108545 at 25°	1.65 at 20°	
Acetone	70.9 at 0°	0.0039496 at 0°	1.26 at 17°–78°	21.85
	73.2 at 20°	0.0030726 at 25°		

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[1] Z. physik. Chem., **12**, 433 (1893) ; **15**, 111 (1894).

[2] *Ibid.*, **14**, 286 (1894).

No such quantitative relation has been worked out for changes in viscosity caused by salts brought into solution, and still less is known about the conductivity which a given salt may be expected to give. Yet Bredig,[1] Wagner[2] and Euler[3] have worked on this problem with considerable success. Wagner found that the viscosity of a salt solution is an additive function of the metallic and non-metallic radicals of the dissolved salt. For allied metals the viscosity decreases as the atomic weight increases. The dissociated ions appear in some cases to have greater, and in other cases less viscosity than the original solution.

To explain this "negative viscosity" shown by certain salts in their power to lower the viscosity of pure water, Euler employed the "Electrostriction theory" proposed by Drude and Nernst.[4] According to this theory the ion is surrounded by a strong electrical field, in virtue of its charge, which causes a strong compression of the liquid in this field. Euler holds that the effect of a salt on viscosity is the result of two tendencies; first, that of the atoms tending to increase the viscosity in inverse proportion to their migration velocities and, second, the electrostriction tending to lessen the viscosity.

Euler has calculated viscosity constants for a large number of ions and finds the relation between them and the migration velocities to be expressed by the formula

$$(\mathrm{A} - 0.68).\mathrm{U} (\text{or } (\mathrm{K} - 0.68).\mathrm{V}) = \text{a constant},$$

where A and K are the viscosity constants and U and V are the migration velocities of the anion and cation, respectively. Hydrogen and hydroxyl ions are exceptions. Some of the values given are the following:

Table III.

Ion.	Migration velocity.	Viscosity constant.
Li	39.8	1.15
Ca	62.0	1.023
K	70.6	0.962
Br	73.0	0.946
NO_3	..	0.919

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[1] Z. physik. Chem., **13**, 243 (1894).

[2] *Ibid.*, **5**, 31 (1890).

[3] *Ibid.*, **25**, 536 (1898).

[4] *Ibid.*, **15**, 79 (1894).

Wagner[1] has shown that Mullenbein's[2] measurements have discounted Euler's explanation of negative viscosity, since the viscosity of the solvent may be lowered by the addition of certain non-electrolytes, even when the viscosity of the dissolved substance is higher than that of the solvent. With ethyl alcohol, *o*-nitrotoluene gives an inversion-point, *m*-nitrotoluene a minimum and *p*-nitrotoluene a maximum.

He proposes, as an explanation, that the solute diminishes the quantity of the solvent in a given space and this leads to a diminution of the viscosity, which diminution is partly compensated, however, by the solute itself. According to the relative magnitude of the various factors, the viscosity may be increased or diminished.

Dunstan[3] has investigated a large number of mixtures. He believes that the increase in viscosity is due to the formation of loosely-held complexes. He thinks that the cause of the minimum of viscosity is more deep-seated than Wagner supposed and attributes it to "some change in molecular aggregation or dissociation."

Blanchard[4] found that the addition of 1 equivalent of ammonia for 1 equivalent of silver, and the addition of 4 equivalents of ammonia for 1 equivalent of copper and zinc in aqueous solutions of their salts, very greatly decreases the viscosity. He reasons that this cannot be due to increased ionization, and therefore rejects the electrostriction theory and proposes a hydrate theory. He says that if the positive ion consists solely of a metallic atom bearing an electric charge, combination with ammonia molecules cannot decrease its mass or readily increase its symmetry, so as to reduce the viscosity. The only explanation seems to be that the ions in solution are hydrated. The hydrate water is replaced by ammonia, which forms with the ion a more stable complex and one of smaller mass, or greater symmetry, or both. He believes that this theory also accounts for negative viscosity and for the effect of pressure on viscosity. Evidently, this is the same conclusion as that reached by Kohlrausch in his hypothesis of ionic spheres, but by a somewhat different method of approach.

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[1] Z. physik. Chem., **46**, 867 (1903).

[2] Dissertation, Leipzig, 1901.

[3] J. Chem. Soc., **85**, 817 (1904). Z. physik. Chem., **49**, 590 (1904).

[4] J. Am. Chem. Soc., **26**, 1315 (1904).

Blanchard added small amounts of water to alcoholic solutions of sodium hydroxide and found the viscosity smaller than would be expected from a study of the pure solvents. This is due, as he thinks, to the formation of a complex between the alkali, water and alcohol, which is, however, smaller or more symmetrical than the alcohol-water complex originally present.

Mixtures of alcohol and water give a maximum of viscosity. Blanchard finds that cupric chloride increases this effect. He further applies this theory to the work of Jones and Lindsay,[1] on conductivity.

The existence of hydrates or solvates (in the case of non-aqueous solvents) in one form or another is an old conception. Poisseuille[2] first suggested it in working with alcohol and water. Graham[3] confirmed and extended Poisseuille's work. Wijkander[4] supposed that acetic acid forms a hydrate with water, $C_2H_4O_2.H_2O$, which would account for abnormal viscosity. The changes due to temperature he attributed to dissociation changes in the liquid. Thorpe and Rodger[5] and Traube[5] also assume the presence of hydrates.

Recently, Varenne and Godefroy[6] have found evidence from viscosity curves for the existence of various hydrates in mixtures of water with methyl and ethyl alcohols and acetone. These are as follows:

Table IV.

Methyl alcohol and water.	Ethyl alcohol and water.	Acetone and water.
$CH_3OH.H_2O$	$C_2H_5OH.2H_2O$	$CH_3COCH_3.3H_2O$
$CH_3OH.2H_2O$	$C_2H_5OH.3H_2O$	$CH_3COCH_3.4H_2O$
$CH_3OH.3H_2O$	$C_2H_5OH.6H_2O$	$CH_3COCH_3.8H_2O$
$CH_3OH.5H_2O$	$3(C_2H_5OH).2H_2O$	$CH_3COCH_3.34H_2O$
$CH_3OH.8H_2O$	$C_2H_6OH.22H_2O$	
$CH_3OH.20H_2O$		

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[1] THIS JOURNAL, **28**, 329 (1902).

[2] *Loc. cit.*

[3] Phil. Trans., **151**, 373 (1861).

[4] Weid. Beibl., 8, 3 (1879).

[5] *Loc. cit.*

[6] Compt. rend., **137**, 992 (1903); **138**, 990 (1904).

This conception of the existence of hydrates differs from the view put forward by Jones,[1] according to which the composition of the hydrates is simply a function of the concentration, the temperature remaining constant. The composition may vary all the way from 1 molecule of water to a large number, every intermediate step being represented. Various lines of evidence have been furnished for this view by Jones,[2] Jones and Getman,[3] and Jones and Bassett.[4] The more important of these have to do with the relation between water of crystallization and lowering of the freezing-point, certain color changes in solution and the relation between water of crystallization and temperature.

(*c*) *Conductivity.*—A great number of researches have been made on conductivity, using a large number of electrolytes and many different solvents. It is necessary to take up only that work which will help to bring out the relation between conductivity and viscosity.

In general, solvents that show abnormal conductivities when electrolytes are dissolved in them, have abnormal viscosities. Dutoit and Aston[5] advanced the idea that dissociating power is related to the amount of polymerization of the solvent, as determined by the surface-tension method of Ramsay and Shields.[6] On the other hand, Euler[7] has shown that potassium iodide and various other salts give considerable conductivity in nitrobenzene and other non-associated or monomolecular solvents, while in butyric and valeric acids, which are highly associated, the conductivity is very small.

The facts as found by Euler support the hypothesis proposed by Thompson[8] and Nernst,[9] which attributes the dissociating power to the high dielectric constant of the medium;

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[1] This Journal, **23**, 89 (1900).

[2] *Ibid.*, **23**, 89 (1900).

[3] Z. physik. Chem., **46**, 244 (1903). This Journal, **31**, 303 (1904). Z. physik. Chem., **49**, 385 (1904).

[4] This Journal, **33**, 584 (1905).

[5] Compt. rend., **125**, 240 (1897).

[6] Z. physik. Chem., **12**, 433 (1893); **15**, 111 (1894).

[7] *Ibid.*, **28**, 619.

[8] Phil. Mag., **36**, 320 (1893).

[9] Z. physik. Chem., **13**, 531 (1894).

but Eversheim,[1] and Walden and Centnerzwer[2] have shown that, although liquid sulphur dioxide has a small dielectric constant, it gives a high conductivity. Therefore, both of these relations hold only approximately.

Plotnikow[3] has shown that the dissociation is dependent somewhat upon the character of the dissolved substance, as well as upon the solvent. He obtained an abnormally great conductivity with the complex compound $AlBr_7CS_2$ in bromine solution, while most salts give little or none. He also obtained a maximum in molecular conductivity with PBr_5 dissolved in bromine, when the composition of the liquid corresponded to the formula PBr_{25}.

Zelinsky and Krapiwin[4] first noted a minimum in conductivity on mixing the solvents methyl alcohol and water. Cohen[5] noted a minimum in dilute solutions of potassium iodide dissolved in mixtures of ethyl alcohol and water. Cohen remarked that either the dissociation in all the mixtures is the same or conductivity is not a measure of dissociation.

Jones and Lindsay[6] worked with binary mixtures of methyl and ethyl alcohols and water. These alcohols and water gave a minimum at low temperatures, in most cases, and a 50 per cent mixture of methyl and ethyl alcohols gave a conductivity less than the mean value for the unmixed solvents. They proposed to account for this by assuming that each of the two associated solvents diminished the association of the other.

Jones and Carroll[7] investigated the conductivity of sodium iodide, cadmium iodide, calcium nitrate and hydrochloric acid, in mixtures of methyl and ethyl alcohols and water. The minimum was observed in all cases at low temperatures. Recalling the hypotheses of Wiedemann, and of Dutoit and Friderich, connecting viscosity and conductivity, they proposed the quantitative relation

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[1] Ann. der Phys., **8**, 539 (1902).

[2] Z. physik. Chem., **39**, 514 (1902).

[3] *Ibid.*, **48**, 220 (1905).

[4] *Ibid.*, **21**, 35 (1896).

[5] *Ibid.*, **25**, 31 (1898).

[6] *Loc. cit.*

[7] This Journal, **32**, 521 (1904).

$$\frac{\mu_v\eta}{x} = \text{constant} \quad \text{or} \quad \frac{\mu_v\eta}{\alpha} = \text{constant},$$

where x is the association factor and α the dissociation. These formulas become $\mu_v\eta$ = constant when $\mu_v = \mu\infty$.

This work has been continued and the relations between the viscosities and conductivities of lithium nitrate, potassium iodide and calcium nitrate, in various mixtures of acetone with methyl alcohol, ethyl alcohol and water have been worked out.

The work of Naumann,[1] on the solubility of salts in acetone, should also be mentioned.

(*d*) *Summary.*—An attempt will be made to sum up, in a brief paragraph, the factors that are already known to influence conductivity.

First, conductivity is dependent upon the number and velocity of the ions and only upon these factors, if we except the small conductivity of salts *per se.* The number of ions present is dependent upon the association factor or upon the dielectric constant of the solvent, and also upon the tendency of the atoms (or groups of atoms) to take up an electric charge, *i. e.*, more or less electro-positive or electro-negative.

The number of ions decreases with rise in temperature and with decreasing concentration. The velocity of the ions is dependent upon the fluidity of the solvent and upon the migration velocity of the ion itself. The fluidity of the solvent is, again, due to its association, to the concentration of the components having constitutive differences, and to the temperature. Pressure also affects the velocity of the ions.

Rise in temperature may decrease the association, or merely drive the molecules farther apart, giving a looser structure. The mobility of the ion is dependent upon its constitution and its affinity for the solvent, tending to produce an atmosphere of greater or less dimensions about itself.

We have not taken into account the result of the attractions between the charges on the ions, but it is not clear that the effect is measurable, and there is some doubt as to whether it is even in the direction indicated by Euler's hypothesis.

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[1] Ber. d. chem. Ges., 37, 4328 (1904).

PART II.

EXPERIMENTAL.

Apparatus.

(*a*) *Conductivity.*—The Kohlrausch method of measuring conductivity, with Wheatstone bridge, telephone receiver and induction coil, was employed. It was not difficult to read to less than 0.1 of 1 per cent. The bridge wire was made of "manganin" and was calibrated before beginning the work. The resistance coils were standardized and found accurate to 0.04 of 1 per cent.

In order to work successfully with acetone, it was necessary to provide cells of special construction, so as to avoid the presence of rubber or wax,[1] which would be dissolved by the solutions. The cells were made of hard glass with ground-glass stoppers and had the form shown in Fig. I. The glass tubes carrying the electrodes were sealed into both the upper and the lower walls of the glass stopper. The distance between the electrodes thus remained permanently fixed.

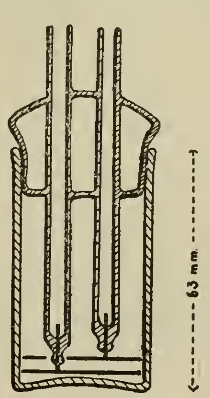

Fig. I.

The zero-bath was prepared by filling a large battery jar with clean, finely crushed ice, moistened with water. This was placed in a pail, made of compressed paper pulp and the annular space filled with finely crushed ice. Thus protected, the bath could be used for a much longer time than with the methods usually employed. The 25° bath was of the usual form, the stirrer being driven by means of a hot-air engine. An Ostwald regulator was employed. The thermometers were regulated to tenths of a degree. They were tested at the beginning of the work. Burettes and flasks were carefully calibrated.

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[1] Jones and Lindsay : *Loc. cit.*

(*b*) *Viscosity.*—The viscometer was of the form recommended by Ostwald.[1] A fixed volume of the liquid to be measured was introduced into the apparatus. The liquid was raised exactly to the mark above the bulb, by air-pressure. The air was dried with sulphuric acid. The pressure was released by means of a Mohr pinch-cock, on a thick-walled rubber tube. By this arrangement the readings agreed to within 0.2 of a second. It was important that the liquids should be given time to drain out of the tube above the upper mark, since, otherwise, a drop of liquid might collect in the upper capillary and impede the entering air, thus introducing large error.

For the zero-bath a battery jar was filled with very finely crushed ice moistened with water. The ice was renewed as often as was necessary to keep the temperature constant. For the 25° bath a 5-liter beaker was employed. The bath was stirred by means of a hot-air engine, the temperature being kept to within 0°.1 of 25°, as in the conductivity method. The room was kept as near this temperature as possible.

We are indebted to Mr. Arthur C. Macy, jeweler, for the loan of a very accurate Waltham stop-watch, reading to two-tenths of a second.

To measure the specific gravities at zero, which was necessary in order to calculate the viscosities, we constructed a pycnometer, Fig. II. (p. 495), which would allow the large expansion of the alcohols and acetone and avoid loss by evaporation.

Preparation of Solutions.

In making up mixtures of solvents, *n* cc. of acetone diluted to 100 cc. was designated as a mixture of "*n* per cent acetone." Since acetone, especially, has a high coefficient of expansion, it was important to have the temperature always the same, 20°. The acetone or alcohol was brought to this temperature before making up the mixture. On mixing acetone and water, contraction took place and heat was generated, so that the mixture was brought to the temperature before diluting to the mark.

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[1] Physiko-chemische Messungen, 2d Ed., p. 260.

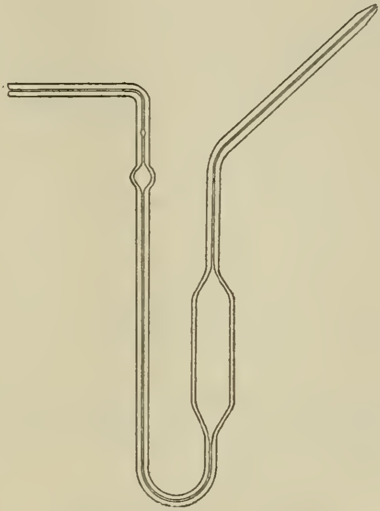

Fig. II.

The mother-solution was made by weighing into a measuring-flask the exact amount of salt required and adding the mixed solvent. Since, however, heat was again generated, especially with the calcium nitrate, the solution was again brought to the designated temperature before diluting to the mark.

From the mother-solution the other solutions were made by successive dilution. Where this would necessitate the use of small quantities of solution, a new mother-solution was made, and from this successive dilutions prepared.

Solvents.

Water.—The water was purified by the method of Jones and Mackay[1] and had a conductivity of 1×10^{-6} at 0°.

Methyl Alcohol.—The methyl alcohol was the best commercial article obtainable. It was boiled with calcium oxide for a day, distilled and allowed to stand over anhydrous copper sulphate for a long time. Before use it was distilled, using a Linnemann fractionating head. Precautions were taken against absorption of moisture. The first and last portions of the distillate were discarded, giving a liquid which boiled constantly at 66°. The mean value of the conductivity was 2×10^{-6} at 25°.

Ethyl Alcohol.—The ethyl alcohol was the best commercial alcohol obtainable. It was purified in the same manner as the methyl alcohol. Its conductivity had a mean value of 2×10^{-6} at 25°.

Acetone.—The acetone was dried over fused calcium chloride for weeks and distilled with a fractionating head as above. Its conductivity was 0.6×10^{-6}.

Conductivity Measurements.

In all determinations of conductivity at least three different resistances were used, and the values given are the mean. However, if the readings did not agree to 0.1 of 1 per cent, they were usually repeated. The constants of the cells were checked at frequent intervals. The cells were not allowed to remain in contact with the solution when not in use, nor to remain empty after being dried out with alcohol and ether. In the former case, small quantities of salt were found to be slowly absorbed and in the latter acetic acid was formed by the action of the platinum on the alcohol or ether in the presence of air. When not in use the cells were filled with pure distilled water.

A N/50 and a N/500 solution of potassium chloride were used in determining the cell constants. The conductivity of the former was taken as 129.7, at 25°. The value of the latter was determined several times in different cells. The mean value obtained agrees well with the interpolated values of other observers.

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[1] Z. physik. Chem., **22**, 237 (1897). THIS JOURNAL, **19**, 91 (1897).

Table V.—Conductivity of N/500 Potassium Chloride at 25°.

Observed value corrected for the conductivity of water	136.5
Corresponding value obtained by Jones and West[1]	135.5
Deduced value, from Kohlrausch[2]	136.94
Interpolated value, from Ostwald[3]	138.7

The temperature coefficients are obtained by dividing the increase in the conductivity per degree, by the conductivity at the lower temperature.

Lithium Nitrate.

The lithium nitrate used in this work was a sample obtained from Kahlbaum. No appreciable impurity could be detected. It was dried in an air-bath at 150° until the weight remained constant. The salt was kept in a desiccator. The operation of drying was repeated whenever the salt was exposed to the air.

Table VI.—Conductivity of Lithium Nitrate in Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	31.17	43.05	0.0154
10	37.62	51.31	0.0145
25	43.40	60.49	0.0158
50	48.31	67.2	0.0157
100	52.0	72.6	0.0155
200	55.1	76.8	0.0147
400	56.8	80.0	0.0172
800	59.6	83.7	0.0162
1200	60.8	85.3	0.0160
1600	61.9	86.7	0.0160

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[1] THIS JOURNAL, 34, 357 (1905).

[2] Leitvermögen der Elektrolyten.

[3] Lehrbuch der allgemeinen Chem., 2d Ed., p. 732.

Table VII.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°	Temperature coefficients.
5	33.50	44.27	0.0128
10	40.78	53.85	0.0128
25	48.36	64.63	0.0134
50	54.29	72.8	0.0136
100	58.9	79.8	0.0148
200	63.6	85.9	0.0140
400	66.2	90.6	0.0147
800	69.8	95.7	0.0148
1200	71.0	97.7	0.0150
1600	73.1	99.8	0.0146

Table VIII.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	32.79	41.26	0.0103
10	41.11	51.68	0.0100
25	51.38	65.39	0.0109
50	58.82	75.42	0.0113
100	65.2	84.8	0.0120
200	69.6	93.2	0.0135
400	75.2	99.2	0.0128
800	80.0	105.3	0.0127
1200	83.3	109.6	0.0126
1600	86.8	112.2	0.0117

Table IX.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	25.53	29.98	0.00703
10	34.06	39.45	0.0158
25	45.86	53.69	0.00683
50	55.50	66.30	0.0078
100	65.2	78.4	0.0081
200	74.8	92.2	0.0093
400	82.6	103.0	0.0099
800	90.0	113.3	0.0103
1200	94.4	119.0	0.0104
1600	96.6	123.6	0.0112

Table X.—Conductivity of Lithium Nitrate in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	7.78	9.25	0.00755
10	9.67	10.87	0.00493
25	11.35	12.86	0.00532
50	14.07	15.64	0.00447
100	18.1	19.5	0.00310
200	23.8	25.3	0.00252
400	30.6	32.4	0.00232
800	43.4	45.5	0.00193
1200	48.7	52.5	0.00311
1600	55.3	59.8	0.00325

Table XI.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	31.17	33.50	32.79	25.53	7.78
10	37.62	40.78	41.11	34.06	9.67
25	43.40	48.36	51.38	45.86	11.35
50	48.31	54.29	58.82	55.50	14.07
100	52.0	58.9	65.2	65.2	18.1
200	55.1	63.6	69.6	74.8	23.8
400	56.8	66.2	75.2	82.6	30.6
800	59.6	69.8	80.0	90.0	43.4
1200	60.8	71.0	83.3	94.4	48.7
1600	61.9	73.1	86.8	96.6	55.3

Table XII.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	43.05	44.27	41.26	29.98	9.25
10	51.31	53.85	51.68	39.45	10.87
25	60.49	64.63	65.39	53.69	12.86
50	67.2	72.8	75.42	66.30	15.64
100	72.6	79.8	84.8	78.4	19.5
200	76.8	85.9	93.2	92.2	25.3
400	80.0	90.6	99.2	103.0	32.4
800	83.7	95.7	105.3	113.3	45.5
1200	85.3	97.7	109.6	119.0	52.5
1600	86.7	99.8	112.2	123.6	59.8

Table XIII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent
5	0.0152	0.0129	0.0103	0.00703	0.00755
10	0.0145	0.0128	0.0100	0.00158	0.00493
25	0.0158	0.0134	0.0109	0.00683	0.00532
50	0.0157	0.0136	0.0113	0.0078	0.00447
100	0.0155	0.0148	0.0120	0.0081	0.00310
200	0.0147	0.0140	0.0135	0.0093	0.00252
400	0.0172	0.0147	0.0128	0.0099	0.00232
800	0.0162	0.0148	0.0127	0.0103	0.00192
1200	0.0160	0.0150	0.0126	0.0104	0.00311
1600	0.0160	0.0146	0.0117	0.0118	0.00325

Tables VI. to XIII. (Figs. III. and IV.) show that lithium nitrate, in mixtures of methyl alcohol and acetone, gives a pronounced maximum in conductivity. At high concentrations the maximum is rather small. As the dilution is in-

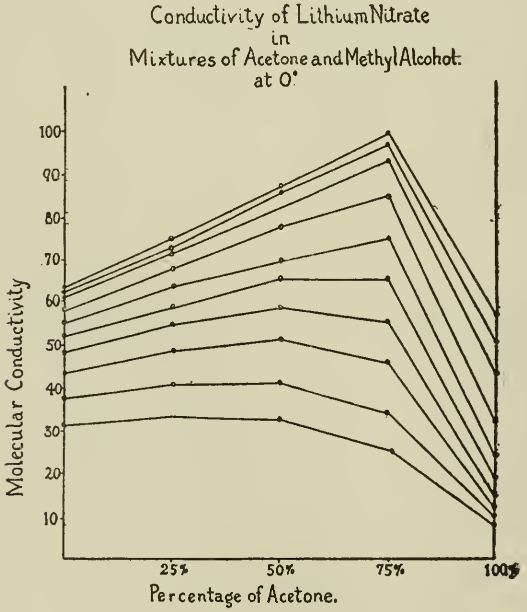

Fig. III.

creased the maximum appears in the 75 per cent mixture and even beyond. It should also be noticed that, in the dilute solutions, the rise in conductivity is directly proportional to the amount of acetone, up to the 75 per cent mixture. The maximum is increased by rise in temperature.

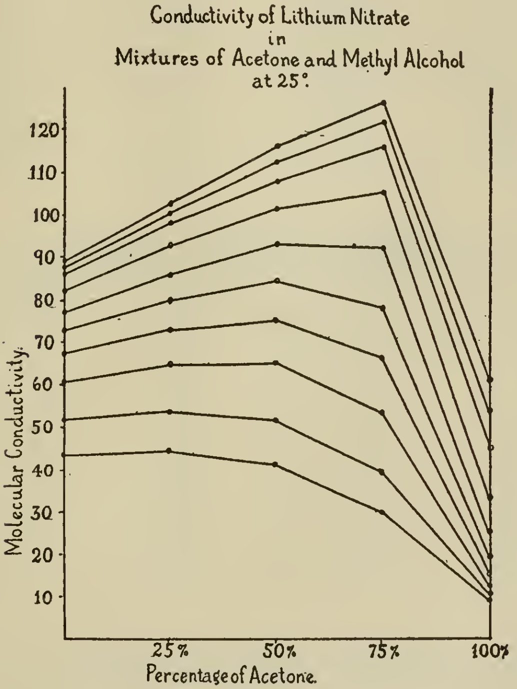

Fig. IV.

The points will be made clear by a study of the figures. In all cases the curves represent the molecular conductivities at the successive dilutions.

Table XIV.—Conductivity of Lithium Nitrate in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	9.14	14.65	0.0241
10	10.75	17.17	0.0238
25	13.55	21.71	0.0240
50	15.54	24.9	0.0241
100	16.9	27.6	0.0251
200	18.4	30.3	0.0260
400	19.1	32.1	0.0271
800	20.3	34.1	0.0251
1200	20.0	34.4	0.0288
1600	21.7	35.4	0.0252

Table XV.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	12.5	18.6	0.0195
10	15.9	22.9	0.0176
25	20.2	29.2	0.0178
50	23.1	33.9	0.0187
100	26.0	38.4	0.0191
200	29.0	43.2	0.0196
400	31.2	46.6	0.0198
800	33.0	50.3	0.0210
1200	34.6	51.8	0.0222
1600	35.1	54.5	0.0220

Table XVI.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	15.2	19.7	0.0142
10	19.6	25.4	0.0119
25	26.1	33.8	0.0118
50	30.9	40.4	0.0123
100	35.7	47.6	0.0133
200	40.4	54.8	0.0142
400	44.4	61.3	0.0152
800	47.4	67.0	0.0165
1200	49.4	69.6	0.0164
1600	50.7	71.9	0.0167

Table XVII.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	14.1	16.9	0.00795
10	19.3	22.5	0.0066
25	27.2	31.3	0.0060
50	34.3	39.7	0.0063
100	41.7	49.6	0.0074
200	50.2	60.1	0.0079
400	54.2	70.8	0.0122
800	64.9	80.9	0.0098
1200	69.5	86.5	0.0098
1600	70.6	91.7	0.0119

Table XVIII.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	9.14	12.5	15.2	14.1	7.78
10	10.75	15.9	19.6	19.3	9.67
25	13.55	20.2	26.1	27.2	11.35
50	15.54	23.1	30.9	34.3	14.07
100	16.9	26.0	35.7	41.7	18.1
200	18.4	29.0	40.4	50.2	23.8
400	19.1	31.2	44.4	54.2	30.6
800	20.3	33.0	47.4	64.9	43.4
1200	20.0	34.6	49.4	69.5	48.7
1600	21.7	35.1	50.7	70.6	55.3

Table XIX.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.65	18.6	19.7	16.9	9.25
10	17.17	22.9	25.4	22.5	10.87
25	21.71	29.2	33.8	31.3	12.86
50	24.90	33.9	40.4	39.7	15.64
100	27.60	38.4	47.6	49.6	19.5
200	30.3	43.2	54.8	60.1	25.3
400	32.1	46.6	61.3	70.8	32.4
800	34.1	50.3	67.0	80.9	45.5
1200	34.4	51.8	69.6	86.5	52.5
1600	35.4	54.5	71.9	91.7	59.8

Table XX.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0241	0.0195	0.0142	0.00795	0.00755
10	0.0238	0.0176	0.0119	0.0066	0.00493
25	0.0240	0.0178	0.0118	0.0060	0.00532
50	0.0241	0.0187	0.0123	0.0063	0.00447
100	0.0251	0.0191	0.0133	0.0074	0.00310
200	0.0260	0.0196	0.0142	0.0079	0.00252
400	0.0271	0.0198	0.0152	0.0122	0.00232
800	0.0251	0.0210	0.0165	0.00985	0.00192
1200	0.0288	0.0222	0.0164	0.0098	0.00311
1600	0.0252	0.0220	0.0167	0.0119	0.00325

Tables XIV. to XX. (Figs. V. and VI.) show the same characteristics for lithium nitrate, in mixtures of acetone and

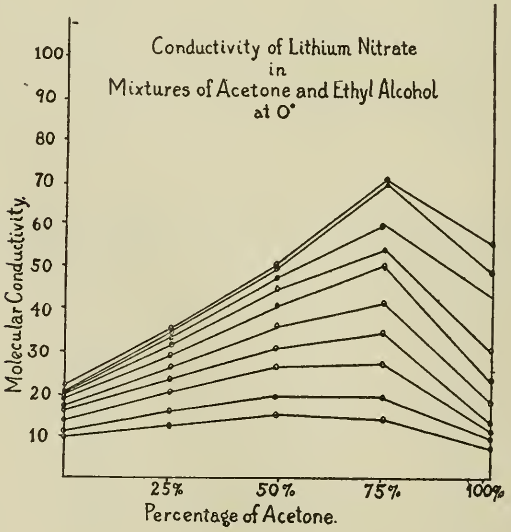

Fig. V.

ethyl alcohol, as those observed for the same salt in mixtures of acetone and methyl alcohol, but there is not such a well-defined maximum in these curves.

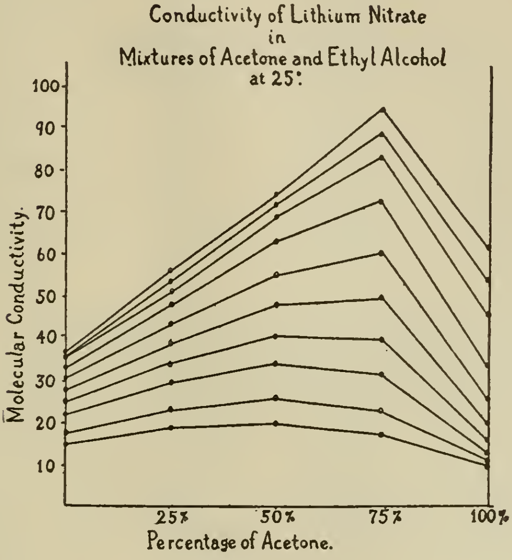

Fig. VI.

Table XXI.—Conductivity of Lithium Nitrate in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	44.45	80.72	0.0323
10	46.39	83.87	0.0323
25	49.57	91.4	0.0334
50	51.4	94.4	0.0334
100	52.5	97.0	0.0340
200	53.1	98.8	0.0342
400	54.3	100.8	0.0341
800	55.0	102.0	0.0340
1200	55.9	102.6	0.0332
1600	56.3	102.8	0.0330
	(58.3)	(107.0)	

Table XXII.—Conductivity of Lithium Nitrate in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	27.31	55.69	0.0415
10	27.37	56.35	0.0421
25	30.32	62.76	0.0427
50	31.50	65.3	0.0430
100	32.8	70.5	0.0460
200	34.1	72.5	0.0450
400	34.6	76.0	0.048
800	37.6	77.8	0.043
1200	39.0	80.7	0.0425
1600	40.0	83.1	0.0430

Table XXIII.—Conductivity of Lithium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	21.81	43.37	0.0394
10	23.48	47.84	0.0415
25	24.90	51.33	0.0425
50	26.26	54.4	0.0427
100	27.2	57.3	0.0442
200	29.1	60.0	0.0425
400	28.8	60.0	0.0433
800	29.9	62.7	0.0440
1200	31.6	65.9	0.0425
1600	32.3	67.5	0.0435

Table XXIV.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	21.25	36.78	0.0292
10	24.41	42.65	0.0298
25	27.64	48.92	0.0308
50	30.25	54.14	0.0316
100	31.8	57.4	0.0322
200	33.5	61.4	0.0333
400	35.1	63.6	0.0325
800	36.7	66.3	0.0322
1200	38.1	68.6	0.0320
1600	37.8	69.1	0.0331

Table XXV.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	44.45	27.31	21.81	21.25	7.78
10	46.39	27.37	23.48	24.41	9.67
25	49.57	30.32	24.90	27.64	11.35
50	51.4	31.50	26.26	30.25	14.07
100	52.5	32.8	27.2	31.8	18.1
200	54.8	34.1	29.1	33.5	23.8
400	54.3	34.6	28.8	35.1	30.6
800	55.0	37.6	29.9	36.7	43.4
1200	55.9	39.0	31.6	38.1	48.7
1600	56.3	40.0	32.3	37.8	55.3

Table XXVI.—Comparison of the Conductivities of Lithium Nitrate in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	80.72	55.69	43.37	36.78	9.25
10	83.87	56.35	47.84	42.65	10.87
25	91.4	62.74	51.33	48.92	12.86
50	94.4	65.3	54.4	54.14	15.64
100	97.0	70.5	57.3	57.4	19.5
200	98.8	72.5	60.0	61.4	25.3
400	100.8	76.0	60.0	63.6	32.4
800	102.0	77.8	62.7	66.3	45.5
1200	102.6	80.7	65.9	68.6	52.5
1600	102.8	83.1	67.5	69.1	59.8

Table XXVII.—Comparison of the Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0323	0.0415	0.0394	0.0292	0.00755
10	0.0323	0.0423	0.0415	0.0298	0.00493
25	0.0334	0.0427	0.0425	0.0308	0.00532
50	0.0334	0.0430	0.0427	0.0316	0.00447
100	0.0340	0.0460	0.0442	0.0322	0.00310
200	0.0342	0.0450	0.0425	0.0333	0.00252
400	0.0341	0.048	0.0433	0.0325	0.00232
800	0.0340	0.043	0.0440	0.0322	0.00192
1200	0.0332	0.0425	0.0425	0.0320	0.00311
1600	0.0330	0.0430	0.0435	0.0331	0.00325

Tables XXI. to XXVII. (Figs. VII. and VIII.) for lithium

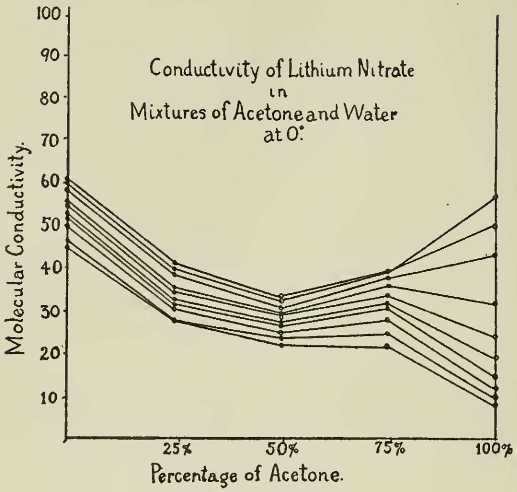

Fig. VII.

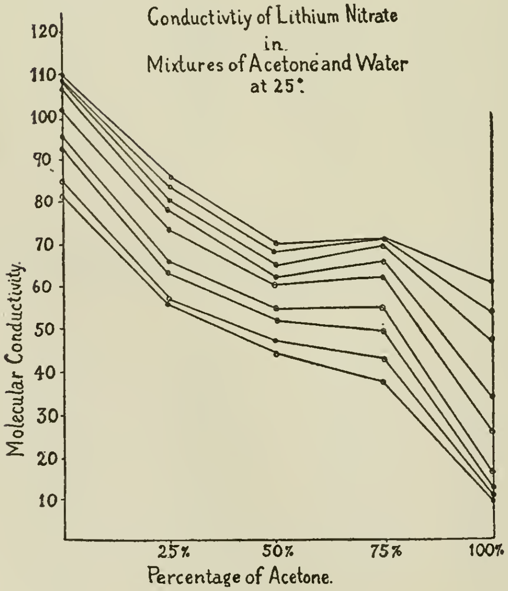

Fig. VIII.

nitrate, in mixtures of acetone and water show, at low temperatures and at high dilution, the minimum which is familiar under similar circumstances in mixtures of the alcohols and water. There is, however, even in this case, a tendency towards a maximum, which results in an inflection-point in most of the curves. It should be especially noticed that the curves diverge from each other rapidly, between the 75 per cent mixture and pure acetone. This seems to indicate that the dissociation is greatly increased by the addition of small amounts of water.

Potassium Iodide.

The salt gave no test for the presence of an iodate and the flame test showed no appreciable impurity. The salt was dried at 100°–110° and kept in a desiccator. The salt dissolved in acetone, giving only a very slight coloration.

Table XXVIII.—Conductivity of Potassium Iodide in Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	65.7	91.4	0.0156
300	68.1	94.6	0.0156
400	68.8	96.3	0.0159
600	70.1	99.0	0.0165
800	70.6	100.5	0.0169
1000	71.1	101.9	0.0174
1200	71.4	102.4	0.0174
1600	71.7	103.3	0.0176

Table XXIX.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	74.1	101.5	0.0148
300	75.6	103.7	0.0151
400	77.6	106.1	0.0147
600	78.1	108.8	0.0157
800	82.3	113.4	0.0151
1000	80.8	113.8	0.0163
1200	82.8	113.8	0.0149
1600	83.9	116.5	0.0155

Table XXX.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	82.7	110.3	0.0133
300	85.2	114.7	0.0139
400	87.2	114.8	0.0127
600	89.6	118.6	0.0129
800	91.9	121.8	0.0130
1000	93.6	123.1	0.0126
1200	93.7	126.2	0.0139
1600	94.1	129.2	0.0149

Table XXXI.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	93.1	117.0	0.0103
300	95.6	123.0	0.0115
400	97.8	124.3	0.0108
600	100.4	129.0	0.0110
800	104.1	131.8	0.0106
1000	103.7	132.7	0.0120
1200	104.3	135.7	0.0118
1600	106.5	137.7	0.0117

Table XXXII.—Conductivity of Potassium Iodide in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	100.4	118.0	0.00701
300	105.8	126.2	0.00772
400	108.9	128.7	0.00730
600	112.3	134.1	0.00775
800	116.2	138.6	0.00772
1000	118.4	141.6	0.00785
1200	118.2	140.3	0.00750
1600	120.0	141.1	0.00704

Table XXXIII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	65.7	74.1	82.7	93.1	100.4
300	68.1	75.6	85.2	95.6	105.8
400	68.8	77.6	87.2	97.8	108.9
600	70.1	78.1	89.6	100.4	112.3
800	70.6	82.3	91.9	104.1	116.2
1000	71.1	80.8	93.6	103.7	118.4
1200	71.4	82.8	93.7	104.3	118.2
1600	71.7	83.9	94.1	106.5	120.0

Table XXXIV.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	91.4	101.5	110.3	117.0	118.0
300	94.6	103.7	114.7	123.0	126.2
400	96.3	106.1	114.8	124.3	128.7
600	99.0	108.8	118.6	129.0	134.1
800	100.5	113.4	121.8	131.8	138.6
1000	101.9	113.8	123.1	132.7	141.6
1200	102.4	113.8	126.2	135.7	140.3
1600	103.3	116.5	129.2	137.7	141.1

Table XXXV.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0156	0.0148	0.0133	0.0103	0.00701
300	0.0156	0.0151	0.0139	0.0115	0.00772
400	0.0159	0.0147	0.0127	0.0108	0.00730
600	0.0165	0.0157	0.0129	0.0110	0.00775
800	0.0169	0.0151	0.0130	0.0106	0.00772
1000	0.0173	0 0163	0.0126	0.0120	0.00785
1200	0.0174	0.0149	0.0159	0.0118	0.00750
1600	0.0176	0.0155	0.0149	0.0117	0.00704

Tables XXVIII. to XXXV. (Figs IX. and X.) for potassium iodide, in mixtures of acetone and methyl alcohol, show that the conductivity is almost exactly what we should expect from the law of averages. There is, however, a slight tendency toward a maximum as we raise the temperature. In this respect the results are similar to those obtained with lithium nitrate. The values for the conductivity of potassium

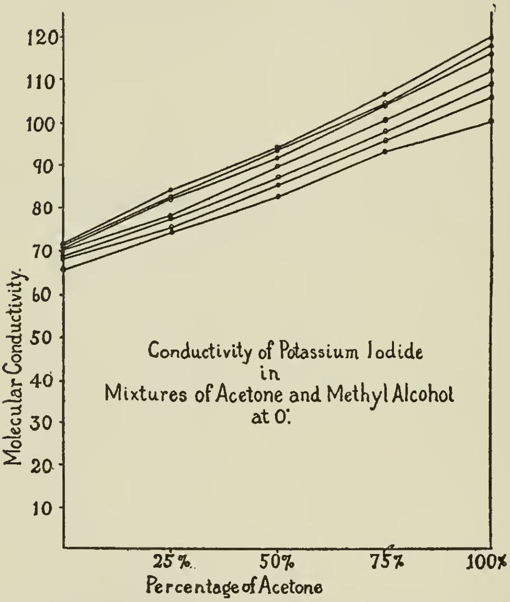

Fig. IX.

iodide in pure water and in ethyl and methyl alcohols were taken from the work of Jones and Lindsay.

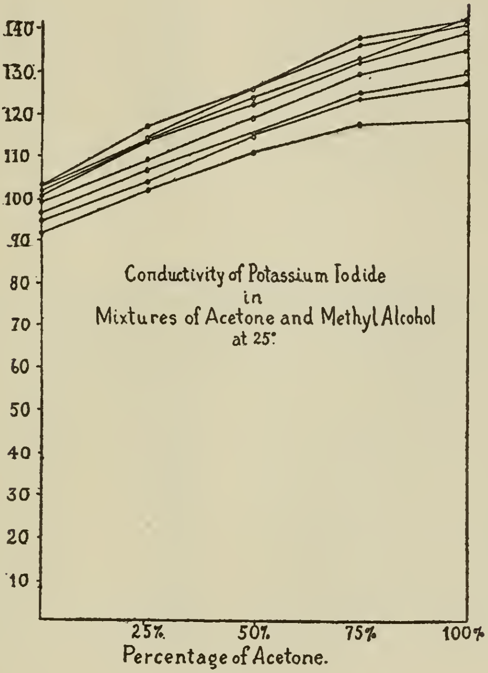

Fig. X.

Table XXXVI.—Conductivity of Potassium Iodide in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	22.0	34.6	0.0230
300	23.2	36.5	0.0241
400	23.8	37.3	0.0238
600	25.5	39.1	0.0212
800	26.2	39.9	0.0209
1000	27.3	41.2	0.0202
1200	27.9	41.8	0.0200
1600	28.6	42.8	0.0194

Table XXXVII.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	35.5	52.5	0.0192
300	36.4	54.2	0.0196
400	37.8	56.3	0.0196
600	38.8	58.0	0.0197
800	40.3	60.5	0.0200
1000	39.8	59.7	0.0200
1200	39.7	60.8	0.0212
1600	40.1	63.5	0.0232

Table XXXVIII.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	52.2	71.4	0.0146
300	53.4	74.0	0.0155
400	56.1	76.8	0.0148
600	57.5	79.1	0.0150
800	59.5	82.6	0.0155
1000	59.7	82.9	0.0155
1200	59.8	82.9	0.0154
1600	61.3	85.4	0.0157

Table XXXIX.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	72.0	92.7	0.0115
300	75.3	97.5	0.0118
400	78.0	100.1	0.0113
600	79.5	102.4	0.0115
800	82.4	106.0	0.0114
1000	81.8	105.4	0.0115
1200	82.7	107.1	0.0118
1600	84.8	109.0	0.0114

Table XL.—Comparison of the Conductivities of Potsasium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	22.0	35.5	52.2	72.0	100.4
300	23.2	36.4	53.4	75.3	105.8
400	23.8	37.8	56.1	78.0	108.9
600	25.5	38.8	57.5	79.5	112.3
800	26.2	40.3	59.5	82.4	116.2
1000	27.3	39.8	59.7	81.8	118.4
1200	27.9	39.7	59.8	82.7	118.2
1600	28.6	40.1	61.3	84.8	120.0

Table XLI.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0° and 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	34.6	52.5	71.4	92.7	118.0
300	36.5	54.2	74.0	97.5	126.2
400	37.3	56.3	76.8	100.1	128.7
600	39.1	58.0	79.1	102.4	134.1
800	39.9	60.5	82.6	106.0	138.6
1000	41.2	59.7	82.9	105.4	141.6
1200	41.8	60.8	82.9	107.1	140.3
1600	42.8	63.5	85.4	109.0	141.1

Table XLII.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0230	0.0192	0.0146	0.0115	0.00701
300	0.0241	0.0196	0.0155	0.0118	0.00772
400	0.0238	0.0196	0.0148	0.0113	0.00730
600	0.0212	0.0197	0.0150	0.0115	0.00775
800	0.0209	0.0200	0.0155	0.0114	0.00772
1000	0.0202	0.0200	0.0155	0.0115	0.00785
1200	0.0200	0.0212	0.0154	0.0118	0.00750
1600	0.0194	0.0232	0.0157	0.0114	0.00704

Tables XXXVI. to XLII. (Figs. XI. and XII.) show the same characteristics for potassium iodide, in mixtures of acetone and ethyl alcohol, as those observed for the same salt in mixtures of acetone and methyl alcohol, but there is less of a tendency towards a maximum. In fact, there is a slight sagging in the curves. It is observed that this statement is

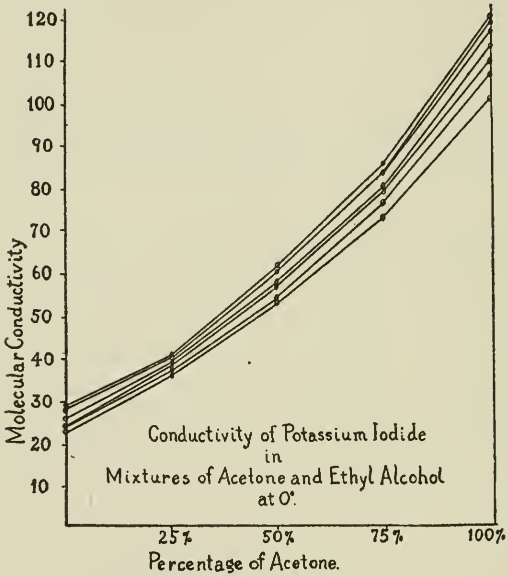

Fig. XI.

almost identical with the one in regard to lithium nitrate in mixtures of acetone and ethyl alcohol (p. 505).

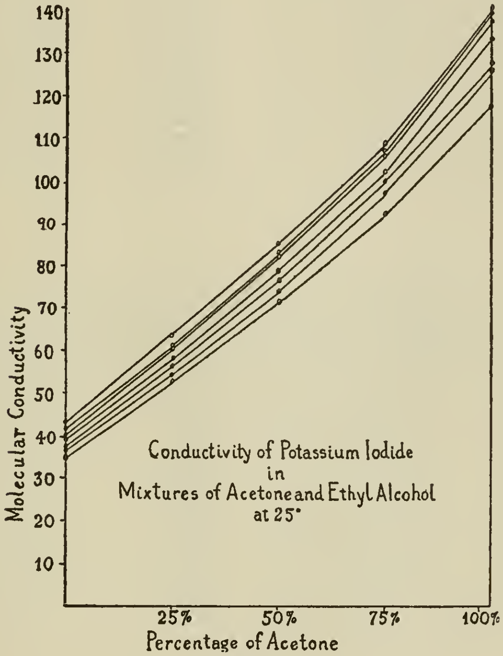

Fig. XII.

Table XLIII.—Conductivity of Potassium Iodide in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	76.7	136.3	0.0310
300	77.2	138.3	0.0316
400	77.5	138.8	0.0318
600	78.0	139.8	0.0312
800	78.0	140.1	0.0318
1000	78.0	140.6	0.0320
1200	78.0	140.7	0.0322
1600	78.0	140.7	0.0322

Table XLIV.—Conductivity of Potassium Iodide in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	44.6	91.1	0.0392
300	44.7	92.7	0.0430
400	45.3	92.4	0.0416
600	46.1	95.6	0.0430
800	47.0	96.9	0.0425
1000	46.3	96.2	0.0432
1200	47.5	102.9	0.0485
1600	47.8	100.1	0.0438

Table XLV.—Conductivity of Potassium Iodide in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	36.3	73.8	0.0413
300	36.8	75.9	0.0425
400	37.2	76.3	0.0420
600	37.6	77.7	0.0427
800	38.6	79.4	0.0423
1000	39.0	80.9	0.0430
1200	38.4	80.6	0.0439
1600	37.5	78.8	0.0440

Table XLVI.—Conductivity of Potassium Iodide in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
200	41.6	74.1	0.0311
300	41.9	74.1	0.0308
400	42.2	74.6	0.0304
600	42.8	75.4	0.0302
800	43.7	79.7	0.0330
1000	42.2	76.4	0.0320
1200	42.8	76.1	0.0310
1600	44.1	79.7	0.0321

Table XLVII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	76.7	44.6	36.3	41.6	100.4
300	77.2	44.7	36.8	41.9	105.8
400	77.5	45.3	37.2	42.2	108.9
600	78.0	46.1	37.6	42.8	112.3
800	78.0	47.0	38.6	43.7	116.2
1000	78.0	46.3	39.0	42.4	118.4
1200	78.0	47.5	38.4	42.8	118.2
1600	78.0	47.8	37.5	44.1	120.0

Table XLVIII.—Comparison of the Conductivities of Potassium Iodide in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	136.3	91.1	73.8	74.1	118.0
300	138.3	92.7	75.9	74.1	126.2
400	138.8	92.4	76.3	74.6	128.7
600	139.8	95.6	77.7	75.4	134.1
800	140.1	96.9	79.4	79.7	138.6
1000	140.6	96.2	80.9	76.4	141.6
1200	140.7	102.9	80.6	76.1	140.3
1600	140.7	100.1	78.8	79.7	141.1

Table XLIX.—Comparison of the Temperature Coefficients of Conductivity of Potassium Iodide in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
200	0.0310	0.0392	0.0413	0.0311	0.00701
300	0.0316	0.0430	0.0425	0.0308	0.00772
400	0.0318	0.0416	0.0420	0.0304	0.00730
600	0.0312	0.0430	0.0427	0.0302	0.00775
800	0.0318	0.0425	0.0423	0.0330	0.00772
1000	0.0320	0.0432	0.0430	0.0320	0.00785
1200	0.0322	0.0485	0.0439	0.0310	0.00750
1600	0.0322	0.0438	0.0440	0.0321	0.00704

Tables XLIII. to XLIX. (Figs. XIII. and XIV.) for potassium iodide, in mixtures of acetone and water, display a minimum in molecular conductivity. There is no tendency towards a maximum. It should, however, be noticed that the divergence of the curves between the 75 per cent mixture and pure acetone is small. The salt is, therefore, quite largely dissociated at all dilutions in all of the mixtures.

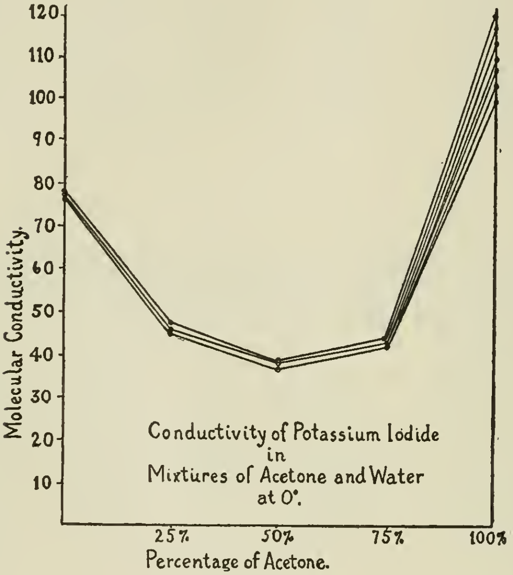

Fig. XIII.

It was thought advisable, at this stage, to use solutions of sodium iodide in the various mixtures. Solutions of sodium iodide in acetone had been investigated by Carrara,[1] Dutoit and Friderich[2] and by Jones.[3] It was noticed, however, that the solution had a high coloration, which deepened on standing. Moreover, there was a slight deposit formed at the same time. On evaporation the residue was still colored. The strongest solutions of the sodium iodide, in acetone, gave a

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[1] Gazz. chim. ital., [1], **27**, 207 (1897).

[2] Bull. Soc. Chim., [3], **19**, 334 (1898).

[3] THIS JOURNAL, **27**, 16 (1902).

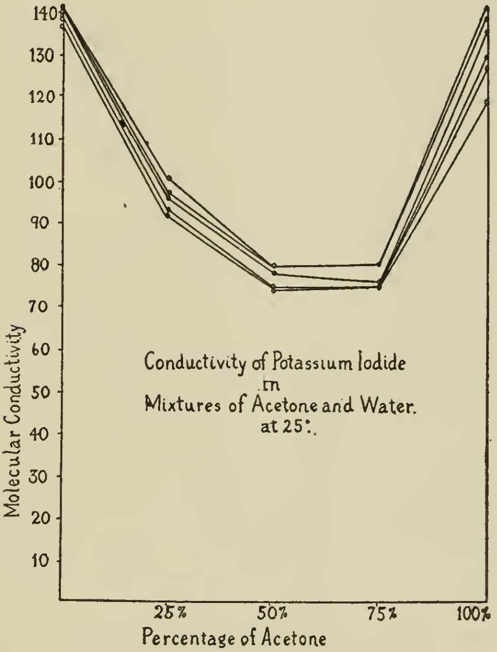

Fig. XIV.

test for iodine with starch paste, while the more dilute solutions, though still somewhat colored, gave none. Free iodine was then added to pure acetone until the same color was reproduced. This solution, tested with starch paste, gave no test for iodine. Time did not permit the further investigation of this interesting point.

Calcium Nitrate.

The calcium nitrate used was an anhydrous preparation obtained from Kahlbaum. It was heated for several days at

140°, until it had a constant weight. Subsequently, it was dried for some time at 140° after each exposure to the air. The salt then contained no calcium oxide, and showed no appreciable impurity by the flame test.

Table L.—Conductivity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 0°. (Carroll.)	μ_v 25°.	μ_v 25°. (Carroll.)	Temperature coefficients.
5	14.33		19.67		0.0149
10	18.98		25.38		0.0135
16				32.79	
25	27.66		36.77		0.0131
32		31.30		41.88	0.0135
50	34.6		45.7		0.0128
64		37.27		50.79	0.0145
100	42.2		55.9		0.0130
128		46.66		60.52	0.0119
200	49.9		65.4		0.0124
256		55.17		73.98	0.0136
400	58.2		75.6		0.0120
800	65.7		86.6		0.0127
1200	74.4		95.0		0.0111
1600	77.2		98.2		0.0109

Table LI.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	13.13	17.36	0.0129
10	17.76	23.08	0.0120
25	26.33	33.74	0.0111
50	33.9	43.2	0.0110
100	42.1	53.9	0.0112
200	50.7	66.8	0.0127
400	60.9	76.8	0.0105
800	71.0	89.4	0.0104
1200	79.7	98.0	0.0092
1600	82.6	102.7	0.0098

Table LII.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	10.16	12.97	0.0111
10	13.82	17.29	0.0100
25	21.30	26.11	0.00903
50	28.11	34.44	0.00895
100	35.7	42.8	0.00795
200	45.2	54.8	0.0085
400	55.3	68.3	0.0088
800	66.8	83.0	0.0097
1200	73.5	91.3	0.0097
1600	79.2	98.8	0.0099

Table LIII.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	6.07	7.65	0.0104
10	8.10	9.78	0.0083
25	12.40	14.56	0.0070
50	16.29	19.47	0.0078
100	21.65	25.1	0.00635
200	28.5	33.0	0.00630
400	38.1	44.3	0.0065
800	49.2	57.8	0.00698
1200	57.3	66.9	0.0067
1600	64.2	75.1	0.0068

Table LIV.—Conductivity of Calcium Nitrate in Acetone at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.93	4.96	0.0105
10	4.44	5.67	0.0111
25	5.06	6.55	0.0118
50	5.34	6.90	0.0117
100	5.48	7.06	0.0115
200	5.93	7.54	0.0109
400	6.69	8.22	0.00916
800	7.93	9.69	0.00884
1200	9.26	11.22	0.00847
1600	10.36	12.62	0.00873

Table LV.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	14.33	13.13	10.16	6.07	3.93
10	18.98	17.76	13.82	8.10	4.44
25	27.66	26.33	21.30	12.40	5.06
50	34.6	33.9	28.11	16.29	5.34
100	42.2	42.1	35.7	21.65	5.48
200	49.9	50.7	45.2	28.5	5.93
400	58.2	60.9	55.3	38.1	6.69
800	65.7	71.0	66.8	49.2	7.93
1200	74.4	79.7	73.5	57.3	9.26
1600	77.2	82.6	79.2	64.2	10.36

Table LVI.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	19.67	17.36	12.97	7.65	4.96
10	25.38	23.08	17.29	9.78	5.67
25	36.77	33.74	26.11	14.56	6.55
50	45.7	43.2	34.44	19.47	6.90
100	55.9	53.9	42.8	25.1	7.06
200	65.4	66.8	54.8	33.0	7.54
400	75.6	76.8	68.3	44.3	8.22
800	86.6	89.4	83.0	57.8	9.69
1200	95.0	98.0	91.3	66.9	11.22
1600	98.2	102.7	98.8	75.1	12.62

Table LVII.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.0149	0.0129	0.0111	0.0104	0.0105
10	0.0135	0.0120	0.0100	0.0083	0.0111
25	0.0131	0.0111	0.00903	0.0070	0.0118
50	0.0128	0.0110	0.00895	0.0078	0.0117
100	0.0130	0.0112	0.00795	0.0063	0.0115
200	0.0124	0.0127	0.0085	0.0065	0.0109
400	0.0120	0.0105	0.0088	0.0065	0.00916
800	0.0127	0.0104	0.0097	0.00698	0.00884
1200	0.0111	0.0092	0.0097	0.0067	0.00847
1600	0.0109	0.0098	0.0099	0.0068	0.00873

Tables L. to LVII. (Figs. XV. and XVI.) for calcium nitrate, in mixtures of acetone and methyl alcohol, give a pronounced maximum in conductivity at high dilutions. It will

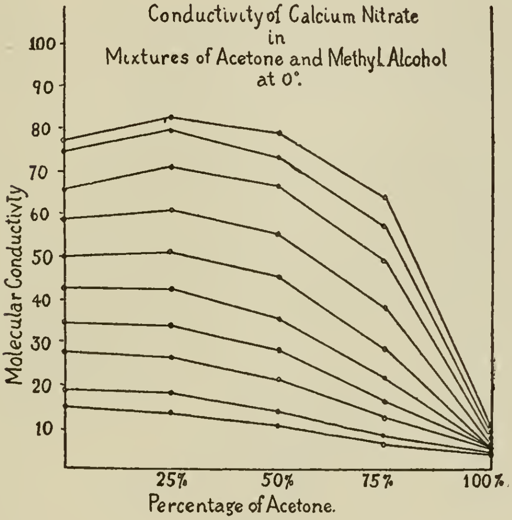

Fig. XV.

be recalled that Jones and Carroll obtained a minimum conductivity with this salt, in mixtures of ethyl alcohol and water, only at low temperatures and at high dilution. It should be noted that calcium nitrate is very slightly dissociated in acetone and that the maximum occurs in the 25 per cent mixture.

The temperature coefficients of conductivity decrease with the dilution, and they are also less in the mixtures than in the pure solvents, the minimum appearing in the 75 per cent mixture.

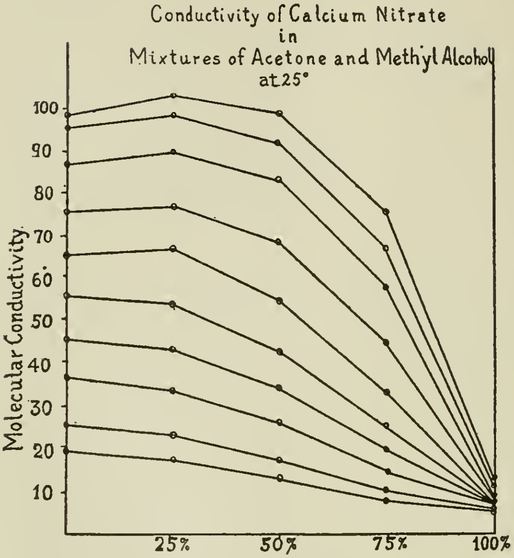

Fig. XVI.

Table LVIII.—Conductivity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.80	5.94	0.022
10	5.13	7.86	0.021
25	7.69	11.67	0.020
50	9.80	14.9	0.024
100	11.9	18.4	0.024
200	14.3	22.4	0.024
400	15.2	23.7	0.022
800	17.2	27.5	0.024
1200	18.1	29.5	0.024
1600	18.8	33.3	0.031

Table LIX.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	4.45	6.18	0.0156
10	6.01	8.29	0.0151
25	9.29	12.52	0.0140
50	12.20	16.59	0.0144
100	15.4	21.1	0.0148
400	22.3	32.2	0.0177
800	27.2	40.1	0.0190
1200	28.9	42.7	0.0191
1600	31.6	46.3	0.0186

Table LX.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	4.42	5.86	0.0130
10	6.00	7.64	0.0109
25	9.25	11.48	0.00963
50	12.33	15.24	0.00945
100	16.1	19.9	0.00942
200	20.7	26.0	0.0102
400	26.1	32.8	0.0102
800	31.8	41.4	0.0121
1200	35.8	46.8	0.0123
1600	38.0	50.7	0.0134

Table LXI.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	3.89	5.08	0.0123
10	4.80	5.99	0.00992
25	6.92	8.22	0.00753
50	9.20	11.34	0.00930
100	12.1	13.8	0.0056
200	16.2	18.3	0.0052
400	21.3	24.3	0.00562
800	28.1	32.7	0.0065
1200	33.2	39.1	0.0073
1600	36.2	42.4	0.0068

Table LXII.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	3.80	4.45	4.42	3.89	3.93
10	5.13	6.01	6.00	4.80	4.44
25	7.69	9.29	9.25	6.92	5.06
50	9.80	12.20	12.33	9.20	5.34
100	11.9	15.4	16.1	12.1	5.48
200	14.3	19.1	20.7	16.2	5.93
400	15.2	22.3	26.1	21.3	6.69
800	17.2	27.2	31.8	28.1	7.93
1200	18.1	28.9	35.8	33.2	9.26
1600	18.81	31.6	38.0	36.2	10.36

Table LXIII.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	5.94	6.18	5.86	5.08	4.96
10	7.86	8.29	7.64	5.99	5.67
25	11.67	12.52	11.48	8.22	6.55
50	14.91	16.59	15.24	11.34	6.90
100	18.4	21.1	19.9	13.8	7.06
200	22.4	26.5	26.0	18.3	7.54
400	23.7	32.2	32.8	24.3	8.22
800	27.5	40.1	41.4	32.7	9.69
1200	29.5	42.7	46.8	39.1	11.22
1600	33.3	46.3	50.7	42.4	12.62

Table LXIV.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	0.022	0.0156	0.0130	0.0123	0.0105
10	0.021	0.0151	0.0109	0.00992	0.0111
25	0.020	0.0140	0.00963	0.00753	0.0118
50	0.024	0.0144	0.00945	0.00930	0.0117
100	0.024	0.0148	0.00942	0.0056	0.0115
200	0.024	0.0155	0.0102	0.0052	0.0109
400	0.022	0.0177	0.0102	0.00562	0.00916
800	0.024	0.0190	0.0121	0.0065	0.00884
1200	0.024	0.0191	0.0123	0.0073	0.00847
1600	0.031	0.0186	0.0134	0.0068	0.00873

Tables LVIII. to LXIV. (Figs XVII. and XVIII.) for calcium nitrate, in mixtures of acetone and ethyl alcohol, show the same characteristics as were observed in the tables for this salt in mixtures of acetone and methyl alcohol, but here the maximum is more prominent, being present at all dilutions and at both temperatures. The dissociation of calcium nitrate in ethyl alcohol, however, is small. With increasing dilution the maximum shifts from the 25 per cent mixture to the 75 per cent mixture.

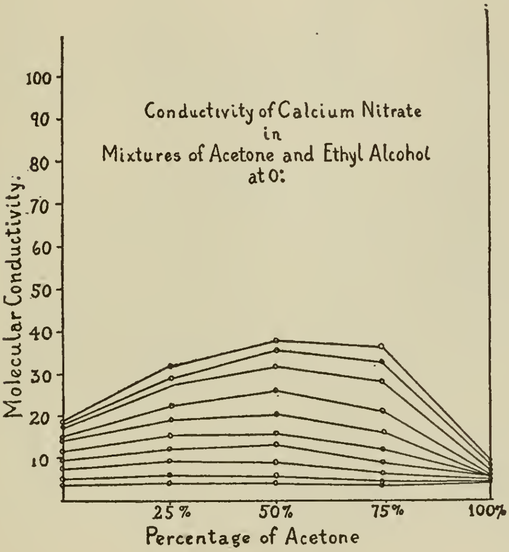

Fig. XVII.

The temperature coefficients in ethyl alcohol are almost constant, perhaps increasing slightly. The temperature coefficients of the mixtures show a minimum in the 75 per cent mixture. A similar phenomenon was noticed in the mixtures of acetone and methyl alcohol.

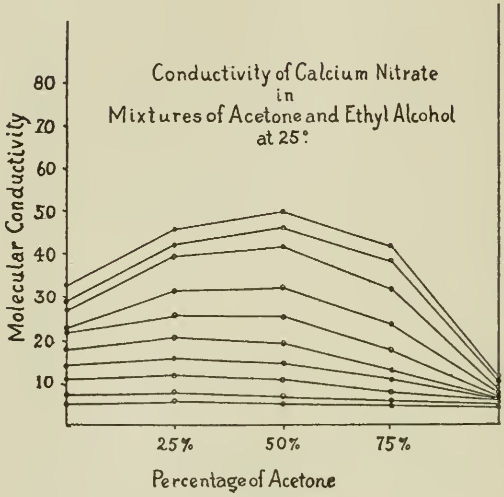

Fig. XVIII.

Table LXV.—Conductivity of Calcium Nitrate in Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	80.3	146.8	0.0331
10	89.8	165.5	0.0333
25	98.2	184.2	0.0350
50	107.0	192.2	0.0313
100	110.4	204.7	0.0341
200	114.9	214.2	0.0343
400	119.9	222.2	0.0341
800	123.4	232.2	0.0351
1200	...	238.5	..
1600	128.3	249.8	0.0378

Table LXVI.—Conductivity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	49.9	101.0	0.0410
10	55.0	112.3	0.0417
25	60.2	123.9	0.0423
50	64.8	134.0	0.0427
100	70.3	144.7	0.0423
200	72.3	154.1	0.0452
400	74.1	154.9	0.0441
800	76.8	161.0	0.0438
1200	79.1	165.4	0.0436
1600	80.0	167.7	0.0439

Table LXVII.—Conductivity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	36.9	73.4	0.0392
10	42.2	84.6	0.0402
25	46.7	94.8	0.0413
50	50.9	104.7	0.0423
100	54.8	115.4	0.0449
200	59.6	120.3	0.0458
400	61.4	128.0	0.0435
800	64.0	133.1	0.0433
1200	66.1	137.9	0.0434
1600	66.2	139.8	0.0444

Table LXVIII.—Conductivity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	μ_v 0°.	μ_v 25°.	Temperature coefficients.
5	25.0	43.1	0.0290
10	31.3	52.8	0.0272
25	40.1	68.3	0.0281
50	45.8	79.2	0.0291
100	52.6	92.3	0.0300
200	58.4	102.5	0.0301
400	62.6	114.9	0.0331
800	71.6	126.9	0.031
1200	75.1	133.5	0.031
1600	76.7	137.7	0.032

Table LXIX.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Water at 0°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	80.3	49.9	36.9	25.0	3.93
10	89.8	55.0	42.2	31.3	4.44
25	98.2	60.2	46.7	40.1	5.06
50	107.0	64.8	50.9	45.8	5.34
100	110.4	70.3	54.8	52.6	5.48
200	114.9	72.3	59.6	58.4	5.93
400	119.9	74.1	61.4	62.6	6.69
800	123.4	76.8	64.0	71.6	7.93
1200	...	79.1	66.1	75.1	9.26
1600	128.3	80.0	66.2	76.7	10.4

Table LXX.—Comparison of the Conductivities of Calcium Nitrate in Mixtures of Acetone and Water at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	148.6	101.0	73.4	43.1	4.96
10	165.5	112.3	84.6	52.8	5.67
25	184.2	123.9	94.8	68.3	6.55
50	192.2	134.0	104.7	79.2	6.90
100	204.7	144.7	115.4	92.3	7.06
200	214.2	154.1	120.3	102.5	7.54
400	222.2	154.9	128.0	114.9	8.22
800	232.2	161.0	133.1	126.9	9.69
1200	238.5	165.4	137.9	133.5	11.2
1600	249.8	167.7	139.8	137.7	12.6

Table LXXI.—Comparison of the Temperature Coefficients of Conductivity of Calcium Nitrate in Mixtures of Acetone and Water from 0° to 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent	100 per cent.
5	0.0331	0.0410	0.0392	0.0290	0.0105
10	0.0333	0.0417	0.0402	0.0272	0.0111
25	0.0350	0.0423	0.0413	0.0281	0.0118
50	0.0313	0.0427	0.0423	0.0291	0.0117
100	0.0341	0.0423	0.0449	0.0300	0.0115
200	0.0343	0.0452	0.0458	0.0301	0.0109
400	0.0341	0.0441	0.0435	0.0331	0.00916
800	0.0351	0.0438	0.0433	0.031	0.00884
1200	..	0.0436	0.0434	0.031	0.00847
1600	0.0378	0.0439	0.0444	0.032	0.00873

Tables LXV. to LXXI. (Figs. XIX. and XX.) for calcium nitrate, in mixtures of acetone and water, show a point of inflection at low temperatures and high dilution. In concentrated solutions, at high temperatures, the conductivity is what we should expect from the law of averages. These results are similar to those obtained with lithium nitrate in mixtures of acetone and water.

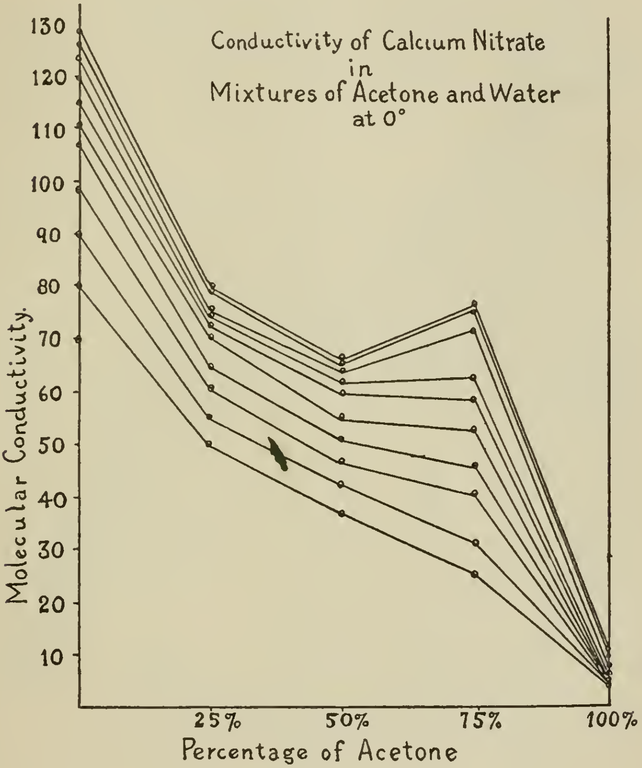

Fig. XIX.

The temperature coefficients of conductivity of water increase with the dilution, while the temperature coefficients of acetone decrease with the dilution. In the 75 per cent mixture the temperature coefficients are nearly independent of the dilution.

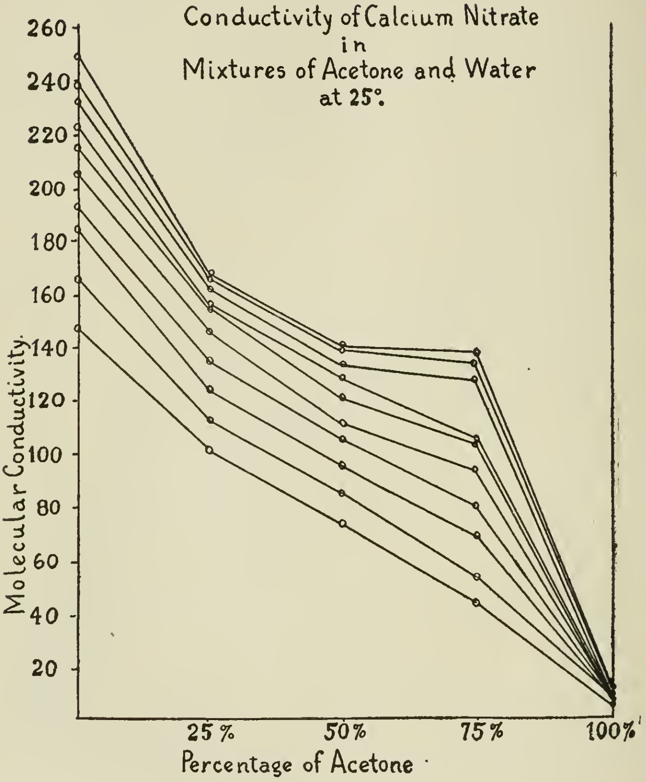

Fig. XX.

Viscosity Measurements.

In the following tables of viscosity data, the values of Thorpe and Rodger[1] for pure water, at 0° and 25°, are taken as the standard and the other values are referred to them ; η represents viscosity, ϕ fluidity and D the density of the liquid in question, at 0° and 25°, compared with the density of water at 0° and 25°, respectively :

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[1] Phil. Trans., 185A, 307 (189&.)

Table LXXII.—Fluidity of Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
Pure solvent	0.01778	56.24	1.000	0.00891	112.3	1.000	0.0426

Table LXXIII.—Fluidity of a Mixture of 25 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
Pure solvent	0.0293	34.12	0.9802	0.001276	78.37	0.9710	0.0518

Table LXXIV.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.01397	71.59	0.948	
1600				0.0133	75.13	0.936	
Pure solvent	0.03027	33.03	0.9522	0.0133	74.96	0.937	0.0508

Table LXXV.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Water at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.009617	104.0	0.892	
1600				0.009019	110.9	0.880	
Pure solvent	0.0170	58.80	0.9023	0.008904	112.3	0.879	0.0364

Table LXXVI.—Fluidity of Calcium Nitrate in Acetone at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.003544	282.1	0.803	
1600				0.003255	307.3	0.790	
Pure solvent	0.004097	244.1	0.8132	0.003237	308.9	0.788	0.0106

Table LXXVII.—Comparison of the Fluidities of Mixtures of Acetone and Water at 0°.

	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Pure solvent	56.2	34.12	33.03	58.80	244.1

Table LXXVIII.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Water at 25°

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10			71.59	104.0	282.1
1600			75.13	110.9	307.3
Pure solvent	112.3	78.37	74.96	112.3	308.9

Table LXXIX.—Fluidity of Calcium Nitrate in Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.006179	161.8	0.804	
1600				0.005543	180.4	0.790	
Pure solvent	0.008185	122.2	0.811	0.005659	176.7	0.790	0.0178

Table LXXX.—Fluidity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.005319	188.0	0.811	
1600				0.004604	217.2	0.790	
Pure solvent	0.006498	153.9	0.816	0.004615	216.7	0.792	0.0163

Table LXXXI.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.004532	220.6	0.816	
1600				0.003926	254.7	0.794	
Pure solvent	0.005336	187.4	0.818	0.003891	257.0	0.794	0.0148

Table LXXXII.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Methyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
10				0.003909	255.8	0.812	
1600				0.003480	287.3	0.793	
Pure solvent	0.004501	222.2	0.817	0.003446	290.1	0.792	0.0122

Table LXXXIII.—Comparison of the Fluidities of Mixtures of Acetone and Methyl Alcohol at 0°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
122.2	153.9	187.4	222.2	244.1

Table LXXXIV.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
10	161.8	188.0	220.6	255.8	282.1
1600	180.4	217.2	254.7	287.3	307.3
Pure solvent	176.7	216.7	257.0	290.1	308.9

Table LXXXV.—Fluidity of Calcium Nitrate in Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficients.
5				0.01373	72.84	0.81612	
Pure solvent	0.01856	53.88	0.80820	0.01106	90.35	0.7895	0.0271

Table LXXXVI.—Fluidity of Calcium Nitrate in a Mixture of 25 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5				0.008444	118.4	0.81822	
Pure solvent	0.01041	96.08	0.81244	0.006714	148.9	0.791	0.0220

Table LXXXVII.—Fluidity of Calcium Nitrate in a Mixture of 50 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5				0.005861	170.6	0.81818	
Pure solvent	0.006801	147.0	0.81394	0.004874	205.2	0.7904	0.0148

Table LXXXVIII.—Fluidity of Calcium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 0° and 25°.

v.	η 0°.	ϕ 0°.	D 0°/0°.	η 25°.	ϕ 25°.	D 25°/25°.	Temperature coefficient.
5				0.004484	223.0	0.81709	
Pure solvent	0.004990	200.4	0.81380	0.003776	264.8	0.7896	0.01296

Table LXXXIX.—Comparison of the Fluidities of Mixtures of Acetone and Ethyl Alcohol at 0°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
53.88	96.08	147.0	200.4	244.1

Table XC.—Comparison of the Fluidities of Calcium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

v.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
5	72.84	118.4	170.6	223.0	263.5
Pure solvent	90.35	148.9	205.2	264.8	308.9

Table XCI.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Water from 0° to 25°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0426	0.0518	0.0508	0.0364	0.0106

Table XCII.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Methyl Alcohol from 0° to 25°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0178	0.0163	0.0148	0.0122	0.0106

Table XCIII.—Comparison of the Temperature Coefficients of Fluidity of Mixtures of Acetone and Ethyl Alcohol from 0° to 25°.

0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0.0271	0.0220	0.0148	0.01296	0.0106

Tables LXXII. to XCIII. (Figs. XXI. and XXII.) show that

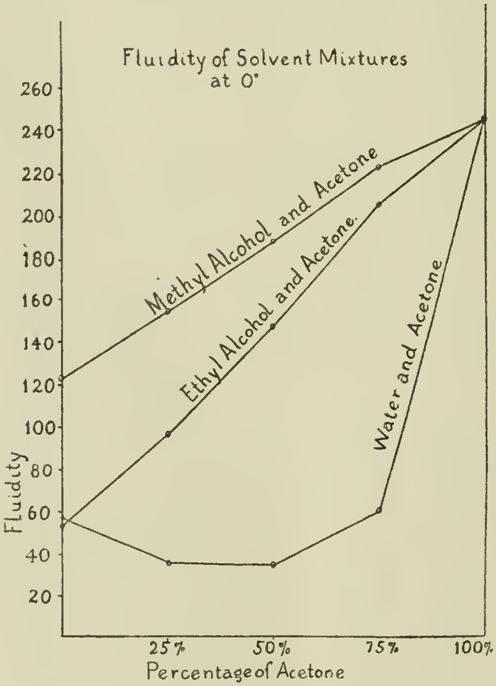

Fig. XXI.

there is a minimum of fluidity only in the case of acetone and water. In the mixtures of acetone with methyl alcohol we get somewhat larger values than would be expected from the fluidities of the pure solvents. This effect is not so apparent, however, in the case of acetone and ethyl alcohol. These last values were compared with those derived from Dunstan's results[1] and were found to be almost identical with them.

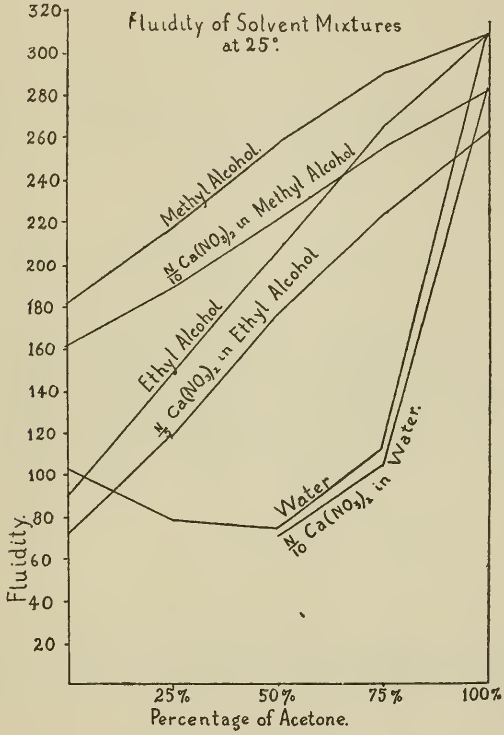

Fig. XXII.

If we compare the viscosity curves of acetone and water with the fluidity curves, we find that the maximum is more pronounced than the fluidity minimum. The viscosity curves for mixtures of acetone and the alcohols show a marked sagging, as Dunstan has pointed out.

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[1] J. Chem. Soc., 85, 821 (1904).

Table XCIV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Water.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Fluidity:						
Pure solv't . . .		0.0426	0.0518	0.0508	0.0364	0.0106
Conductivity:						
5	$Ca(NO_3)_2$	0.0331	0.0410	0.0392	0.0290	0.01050
1600	"	0.0378	0.0439	0.0444	0.0320	0.00873
5	$LiNO_3$	0.0323	0.0415	0.0394	0.0292	0.00755
1600	"	0.0330	0.0430	0.0435	0.0331	0.00325
200	KI	0.0310	0.0392	0.0413	0.0311	0.00701
1600	"	0.0322	0.0438	0.0440	0.0321	0.00704

Table XCV.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Ethyl Alcohol.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Fluidity:						
Puresolv't . .		0.0271	0.0220	0.0148	0.01296	0.0106
Conductivity:						
5	$Ca(NO_3)_2$	0.022	0.0156	0.0130	0.0123	0.0105
1600	"	0.031(?)	0.0186	0.0134	0.0068	0.00873
5	$LiNO_3$	0.0241	0.0195	0.0142	0.00795	0.00755
1600	"	0.0252	0.0220	0.0167	0.0119	0.00325
200	KI	0.0230	0.0192	0.0146	0.0115	0.00701
1600	"	0.0194	0.0232	0.0157	0.0114	0.00704

Table XCVI.—Comparison of the Temperature Coefficients of Conductivity and Fluidity in Mixtures of Acetone and Methyl Alcohol.

v.	Solute.	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
Fluidity:						
Pure solv't	. . .	0.0178	0.0163	0.0148	0.0122	0.0106
Conductivity:						
5	$Ca(NO_3)_2$	0.0149	0.0129	0.0111	0.104	0.0105
1600	"	0.0109	0.0098	0.0099	0.0068	0.00873
5	$LiNO_3$	0.0152	0.0129	0.0103	0.0104	0.00755
1600	"	0.0160	0.0146	0.0117	0.0112	0.00325
200	KI	0.0156	0.0148	0.0133	0.0103	0.00701
1600	"	0.0176	0.0155	0.0149	0.0117	0.00704

Tables XCIV. to XCVI. show that although the temperature coefficients of conductivity and fluidity vary in the same manner, yet the former are uniformly smaller than the latter.

Discussion of Experimental Results.

The curves for the conductivity of potassium iodide in all of the different mixtures, are very similar to the curves of fluidity in the corresponding mixtures. Lithium nitrate and calcium nitrate in all mixtures, at low temperatures, show a deviation from the fluidity curves, particularly in the 75 per cent mixtures, tending to produce a maximum in conductivity.

The work of Jones and Lindsay[1] and of Jones and Carroll[1] showed that solutions of lithium nitrate, in mixtures of methyl alcohol and water, gave curves with a simple minimum, like the fluidity curves for the corresponding mixtures. Calcium nitrate, dissolved in the same mixtures and also in mixtures of ethyl alcohol and water, in no case gave a minimum according to Jones and Carroll,[1] consequently, their curves are not similar to the corresponding fluidity curves.

Our results differ fundamentally from those heretofore observed, in that the mixtures of acetone with the alcohols and water show a tendency towards a maximum in the conductivity of solutions of certain salts, such as lithium nitrate and calcium nitrate.

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[1] *Loc. cit.*

PART III.

Discussion of Results.

Since conductivity is dependent upon fluidity, and not *vice versa*, we will first discuss the fluidity curves and then the conductivity curves in connection with them.

When methyl alcohol or ethyl alcohol is mixed with acetone the fluidity curve of the mixtures is a straight line. This is what we should expect, if the fluidity of each of the components has its proportionate effect. Hence, we may conclude that the molecular aggregations of these pure solvents are not essentially changed in regard to size (or symmetry) by mixing the two solvents. We have already shown that the work of Thorpe and Rodger,[1] Traube,[1] Varenne and Godefroy[1] and others has made it evident that viscosity is dependent upon the character of the molecular aggregations present.

It may be objected that a straight line is not the "normal" fluidity curve, since, heretofore, a straight line has been considered to be the normal viscosity curve and the two conceptions are, in general, incompatible. To make this clear, let us suppose that we mix two liquids which are made up of particles which have no unusual action on each other, *i. e.*, do not form new aggregations of any kind. Two monomolecular liquids which do not form complexes on mixing would fulfil this condition. Further, let us suppose that the liquid is allowed to flow through a tube. The resulting fluidity would be the sum of the partial fluidities of the components. That is, the more rapidly moving particles would be held back by the slower ones, and the motion would be a mean value, proportional to the relative amounts of the components. Formulated this would be

$$(m_1 + m_2)\phi = m_1\phi_1 + m_2\phi_2 \quad \ldots \ldots \quad (1),$$

where m_1 and m_2 are the amounts of the components, and ϕ_1 and ϕ_2 are their respective fluidities.

This is similar to the conception which we have in electricity, where the conductance of two or more conductors is represented by the sum of their separate conductances. The conductance of a single conductor is expressed by the value

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[1] *Loc. cit.*

$$\frac{c\ \sigma}{l},$$

where c is the specific conductivity, σ the cross-section of the conductor and l the length. The conductance of a pair of conductors of different material, in parallel, is, per unit length,

$$(\sigma_1 + \sigma_2)c = c_1\sigma_1 + c_2\sigma_2.$$

Admitting this reasoning, it becomes evident that conductivity and fluidity are strictly comparable.

It will be noticed, moreover, that the *viscosities are not additive.*

If η_1 and η_2 represent the viscosities of the two components, then, since viscosity is the reciprocal of fluidity, we have from (1):

$$(m_1 + m_2)\frac{1}{H} = \frac{m_1}{\eta_1} + \frac{m_2}{\eta_2}.$$

By making m_1 and m_2 the percentages of the respective components:

$$\frac{1}{H} = \frac{m_1}{\eta_1} + \frac{1 - m_1}{\eta_2}$$

$$\eta_1\eta_2 = [m_1\eta_2 + (1 - m_1)\eta_1]H$$

$$= [m_1(\eta_2 - \eta_1) + \eta_1]H \quad . \ . \ . \ . \ . \ . \ . \ . \ (2).$$

Now let

$$m_1(\eta_2 - \eta_1) + \eta_1 = m'_1(\eta_2 - \eta_1)$$

then

$$m'_1 = m_1 + \frac{\eta_1}{\eta_2 - \eta_1}.$$

Substituting this value in (2),

$$m'_1 H = \frac{\eta_1\eta_2}{\eta_2 - \eta_1} = \text{constant},$$

which is the equation of the equilateral hyperbola, the Y-axis of which is a distance $\frac{\eta_1}{\eta_2 - \eta_1}$ to the left of the origin, to which equation (1) is referred.

Thus, we seem justified in concluding that *the hyperbola is the normal curve for viscosities.*

From the above considerations we are led to the belief that inferences made from viscosity curves alone may lead to erroneous conclusions. For example, Wijkander[1] reached the conclusion that in no case is the viscosity identical with that calculated by the admixture rule. In the case of mixtures of ether with chloroform and of ether with carbon disulphide, there were inflection-points in the curves, but no simple relation between the viscosity coefficients of a mixture and those of its constituents could be deduced.

Linebarger[2] found that the observed viscosities, in general, were less than those calculated by the mixture rule, except, perhaps, in the case of mixtures of benzene and chloroform and mixtures of carbon disulphide and benzene, toluene, ether and acetic ether, where, according to Dunstan, the temperature of observation, 25°, was possibly too near the boiling-point of the carbon disulphide to make any specific influence which that liquid might exert at lower temperatures perceptible.

Dunstan[3] makes the significant statement that "the law of mixtures is never accurately obeyed, and divergences seem to be more clearly marked in the case of viscosity than with other properties, such as refractive index."

These discrepancies are explained if our view be accepted, since the divergence in every abnormal case thus far investigated is smaller for the fluidity curves than for the corresponding viscosity curves, and the mixtures with carbon disulphide, which give "normal" viscosity curves, also give *fluidity* curves that are equally satisfactory. In the particular case of acetone and methyl alcohol or ethyl alcohol, the fluidity is a straight line, nearly to within the limits of experimental error, so these two pairs of liquids may be considered as perfectly normal.

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[1] Weid. Beibl., 8, 3 (1879).

[2] Am. J. Sci., [4], 2, 331 (1896).

[3] J. Chem. Soc., 85, 817 (1904). Z. physik. Chem., 49, 590 (1904).

It must be stated explicitly that many of the conclusions of the above-mentioned workers are not changed by this new method of comparison of results, especially since, in many cases, they obtained curves with actual maxima and minima. These effects are reproduced in the fluidities as minima and maxima, respectively, which are generally less prominent than before.

A separate paper will be published in the near future, dealing with some of the recorded viscosity data from this new point of view.

When most of the organic solvents worked with up to this time are mixed with water, there is a very large increase in viscosity. In general, there is also a contraction on mixing these solvents and water. Some of those that give a pronounced maximum of viscosity are methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, acetic acid, propionic acid, butyric acid, isobutyric acid and acetone. The workers in this field have attributed the increase in viscosity to increase in the size of the molecular aggregations.

This decrease in fluidity retards the movement of the ions, hence there is a fall in molecular conductivity, which explains the minimum in conductivity heretofore observed by Zelinsky and Krapiwin,[1] Cohen,[1] Jones and Lindsay,[1] Jones and Carroll[1] and ourselves. This relation between viscosity and conductivity, as has been shown, has long been recognized. Wiedemann,[1] Stephan, Dutoit and Friderich and Jones and Carroll have been connected with the development of the exact relation between them.

If the salt happens to be highly dissociated in water and very little dissociated in the other solvent, the curves may be at such an angle with the axis of X that there will be only a sagging of the curve and not an actual minimum. Therefore, the *amount of deviation from the normal curve* appears to us to be a matter of prime importance, while the finding of a *minimum* is not.

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[1] *Loc. cit.*

If we could make a correction at the different parts of the curve for the different degrees of dissociation in the pure solvents and in the mixtures, we should then have a curve exactly parallel to the fluidity curve, if it is true that fluidity and dissociation are the only factors concerned, as Dutoit and Friderich and Jones and Carroll supposed. In our case it is almost impossible to make the correction with the data at hand, except, possibly, in the case of potassium iodide. The conductivity values for potassium iodide show that it is nearly dissociated in all mixtures, but with the other salts complete dissociation is not even approximately reached. Thinking that it might be possible to calculate $\mu\infty$, we have tested Kohlrausch's formula,

$$\frac{\mu\infty - \mu_v}{C\ ^1\!/_3} = K,$$

where C is the concentration and K is a constant. We found that it did not apply except in aqueous solutions. Völlmer[1] has already shown that the Ostwald dilution law does not apply to solutions in ethyl alcohol and methyl alcohol. Solutions of potassium iodide, in mixtures of methyl alcohol and water, were investigated by Zelinsky and Krapiwin and Jones and Lindsay. The conductivity curves resemble the fluidity curves for methyl alcohol and water, as shown by Jones and Carroll. We have found the same similarity in the case of potassium iodide and water.

If we accept Kohlrausch's hypothesis of ionic spheres, it is evident that the atmosphere about the ions remains of the same size throughout all the mixtures; otherwise the ions would tend to show a maximum in conductivity in those mixtures where the atmosphere is smallest, causing a divergence from the fluidity curves. Difference in dissociation would also cause a divergence between the conductivity and fluidity curves. In the above case, however, the dissociation is large and all the curves are parallel.

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[1] Ann. der Phys., **52**, 328 (1894).

If we pass now to potassium iodide in mixtures of acetone with methyl alcohol and ethyl alcohol, we find, again, that the conductivity curves and fluidity curves are very similar, *i. e.*, nearly straight lines, with a tendency towards a maximum, which is greater in the case of methyl alcohol than in that of ethyl alcohol. Evidently the changes in the size of the ionic spheres and the changes in the dissociation have either counteracted each other or remained zero.

Now let us consider lithium nitrate. In mixtures of acetone with the alcohols, we get a pronounced maximum in conductivity in the 75 per cent mixtures, at high dilutions. Since these solvents gave no such minimum in the case of potassium iodide, the maximum must be connected with the lithium nitrate itself. There are two possible explanations of the phenomenon: (1) Increase in dissociation in the 75 per cent mixture; (2) increase in the mobility of the ions, due to the diminution in the size of the ionic spheres. We shall attempt to decide between these two possibilities.

We have shown by consideration of the fluidities, that the liquids are not more associated in the mixtures than in the pure solvents, hence, if we accept the hypothesis of Dutoit and Aston, that dissociation power increases with the association of the solvent, the maximum cannot be due to increase in dissociation in the mixture. For example, calcium nitrate shows a pronounced maximum in conductivity in mixtures of alcohol and acetone, even though the dissociation of calcium nitrate in pure acetone is very small. It hardly seems probable that the acetone increases the dissociation of pure alcohol if it does not form complexes with it. We also have the fact, found by Jones and Carroll, that even in the case of alcohol and water, where molecular aggregations are known to be formed, there is not an increase in dissociation larger than the possible experimental error. Furthermore, if the 75 per cent mixture has the highest dissociating power, we should not expect to find the maximum migrating from the 25 per cent mixture to beyond the 75 per cent mixture, as the concentration of the dissolved substance decreases. This is the case with lithium nitrate, in mixtures of the alcohols and acetone. Finally, the maximum in conductivity should manifest itself in the most concentrated solutions of potassium iodide, in mixtures of acetone with the alcohols. This is contrary to the facts. We, therefore, accept, tentatively, the view that *the maximum in conductivity is due, primarily, to a change in the dimensions of the ionic spheres.*

The determination, however, of the dissociation of lithium nitrate in pure alcohol, in pure acetone and in a 75 per cent mixture of these solvents, would be a very important check. Through the kindness of Mr. L. McMaster this point has been tested for acetone and ethyl alcohol, as shown in the table below:

Table XCVII.—Conductivity of Lithium Nitrate in Pure Acetone at 25°.

v.	μ_v 25° corrected.
2000	55.28
2500	62.87
3000	66.42

Table XCVIII.—Conductivity of Lithium Nitrate in a Mixture of 75 Per Cent Acetone and Ethyl Alcohol at 25°.

v.	μ_v 25° corrected.
2000	92.66
2500	100.55
3000	101.88

Table XCIX.—Conductivity of Lithium Nitrate in Pure Acetone at 25°.

v.	μ_v 25° corrected.
2000	37.01
2500	41.04
3000	41.48

The conductivity of the pure acetone used in these experiments was 1.516×10^{-6}; that of the pure alcohol 0.857×10^{-6}.

These results show that complete dissociation is nearly reached only in the pure alcohol, and that the mixture is dissociated about as we might expect from the law of averages. We note that the maximum is very pronounced.

The conclusions of Dutoit and Friderich and of Jones and Carroll, that conductivity is inversely proportional to the viscosity and directly proportional to the association factor of the solvent (or to the amount of dissociation), are incomplete. It fails to take into consideration changes in the dimensions of the ionic spheres.

In the conductivities of lithium nitrate, in mixtures of acetone and water, the decreased fluidity manifests itself again. We notice, however, that the power of the acetone to produce smaller (or more symmetrical) ionic spheres is not destroyed by substituting water for methyl alcohol or ethyl alcohol. Practically all of the dilutions in the 75 per cent mixture of acetone and water show a decided elevation of the conductivity curves above those we should expect from similar measurements with potassium iodide. That increase in dissociation would make itself manifest in this way is doubtful, and our theory is thus strengthened.

Jones and Lindsay's results with lithium nitrate, in mixtures of water and methyl alcohol, do not show this effect, hence the acetone acts peculiarly in this respect. However, acetone behaves exceptionally in other ways.

At this point we should call attention to the fact that lithium forms à very slowly moving ion, *i. e.*, one with a large ionic sphere, while potassium forms a comparatively rapidly moving ion, *i. e.*, one with a small ionic sphere. The anions used do not differ greatly. Calcium forms an ion with a migration velocity between that of lithium and potassium. It was thought best to measure the conductivities of calcium nitrate in all of the mixtures, exactly as with the other salts.

The results show that the tendency towards a maximum in conductivity in the mixtures is very marked indeed. Moreover, they show that calcium nitrate is dissociated in the solvents very differently from lithium nitrate. Calcium nitrate is dissociated to a large extent in water and methyl alcohol, very much less in ethyl alcohol and still less in acetone. In spite of all differences, we are struck by the fact that the maximum *divergence* still tends to manifest itself in the 75 per cent mixture. Especially is this the case with acetone and water.

Let us now turn our attention to the concentrated solutions. In these we find the tendency towards a maximum very small, or entirely absent. If our explanation is correct, then, as the concentration of the salt increases, there will be less of the solvent for the formation of ionic spheres or, in the case of mixtures which tend to reduce the large atmospheres of the dilute solutions, the mass action of the solvent is much diminished.

Calcium nitrate is intermediate in its behavior between potassium iodide and lithium nitrate. It seems reasonable to connect this with the migration velocity. It would be interesting to experiment with sodium, the ion of which has a slow migration velocity, but, as we have shown, sodium iodide, although soluble, is unsuited for this purpose.

Summary.

We have measured the fluidities of mixtures of acetone with methyl alcohol, ethyl alcohol and water and of a few solutions of calcium nitrate in these mixtures.

We have measured the conductivity of various concentrations of lithium nitrate, potassium iodide and calcium nitrate, dissolved in the above mixtures.

These conductivities, in the case of mixtures of acetone and water, exhibit the minimum in conductivity previously observed by several other workers. Moreover, this minimum in conductivity has been shown to be intimately connected with the minimum in fluidity observed in these mixtures, but the conductivity curves of different salts show marked differences.

In the mixtures of acetone and the alcohols, the fluidities are what we should expect from the law of averages, *i. e.*, the fluidity curve is nearly a straight line. From this fact we have concluded that acetone and the alcohols thus far studied do not form more complex molecular aggregations when mixed than were originally present before mixing.

The conductivities of potassium iodide, in mixtures of acetone with methyl alcohol or ethyl alcohol, are also what we should expect from the law of averages—the conductivity curves are nearly straight lines at all dilutions. Again, the conductivity has been shown to be intimately connected with fluidity.

Lithium nitrate and calcium nitrate, however, give a very pronounced *maximum in conductivity*, in mixtures of acetone with methyl alcohol or ethyl alcohol. Evidently this was an unexpected phenomenon; to explain it all of the factors that could reasonably influence conductivity were collected. After the elimination of several of them, the possible explanations were shown to be either in an increase in dissociation, giving rise to more ions, or in a diminution in the size of the ionic spheres already in the solution.

It was then shown to be possible to eliminate one of these factors by the following considerations:

1. The fluidity of the mixtures of acetone and alcohol shows that there is no increase in molecular aggregation, hence, we should not expect increased dissociation, if we accept the hypothesis of Dutoit and Aston.

2. Jones and Carroll have shown that, even in the case of alcohol and water, there is practically no increase in dissociation in the mixtures.

3. Furthermore, the maximum migrates from the 25 per cent mixture, at high concentration, to the 75 per cent mixture in the more dilute solutions. This would hardly be expected if the dissociating power is greatest in a certain mixture.

4. Potassium iodide shows no tendency towards a maximum of conductivity in the most concentrated solution with which we worked.

5. Very recent measurements, at extreme dilution, have failed to show any great difference in the dissociating power of the mixtures from that of the pure solvents.

We, therefore, seemed justified in the conclusion that the maximum in conductivity is due to a change in the dimensions of the atmospheres about the ions.

The conclusion of Dutoit and Friderich and of Jones and Carroll, that conductivity is proportional to the dissociation, and inversely proportional to the viscosity, has been shown to be incomplete in not taking into consideration possible changes in the size of the ionic spheres.

The conductivities of lithium nitrate and calcium nitrate, in mixtures of acetone and water, again show a tendency towards a maximum, in spite of the great diminution in fluidity.

Finally, it has been pointed out that the tendency to form a maximum in conductivity increases from potassium iodide, through calcium nitrate, to lithium nitrate, which seems to show these effects most strongly. This may be connected with the migration velocities of these ions.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
May, 1905.

Contributions from the Sheffield Laboratory of Yale University.

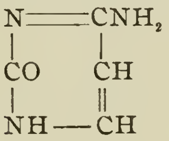
CXXVII.—RESEARCHES ON PYRIMIDINES: ON 2,5-DIAMINO-6-OXYPYRIMIDINE.

[TWELFTH PAPER.]

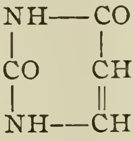
BY TREAT B. JOHNSON AND CARL O. JOHNS.

In a paper by Wheeler and Johnson[1] on 5-methylcytosine it was stated that work on the preparation of oxydiaminopyrimidines would be carried on in this laboratory. These particular pyrimidine derivatives are of especial interest because of the fact that Kutscher[2] believes he isolated such a compound, in the form of its picrate, from yeast nucleic acid. Kutscher considers that a similar analogy exists between his unknown base and cytosine as exists between thymine and uracil. While thymine differs from uracil by a methyl radical, he thinks that his new base differs from cytosine by an amino group.

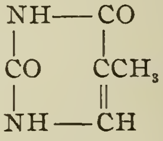
The pyrimidine derivatives that have hitherto been isolated from the decomposition-products of nucleic acid have been mono-oxy or di-oxy derivatives, in which the oxygen atoms occupy position 2 as in cytosine, I., or both positions 2 and 6 as in uracil, II., and thymine, III.:



I.



II.



III.

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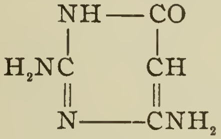
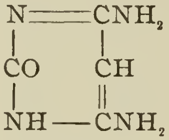
[1] THIS JOURNAL, 31, 592 (1904).

[2] Z. physiol. Chem., 38, 176 (1903).

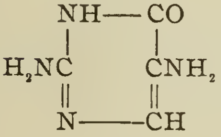
It appears to the writers that if Kutscher's base is an oxydiaminopyrimidine, of all the possible diamino derivatives, the most probable forms to be considered are likewise those in which the oxygen atom occupies either position 2 or 6. An examination of the following formulas will show that the only oxydiamino derivatives that fulfil these conditions, assuming that the amino groups are attached to carbon, are: 6-oxy-2,4-diaminopyrimidine, IV., 2-oxy-4,6-diaminopyrimidine, V., 6-oxy-2,5-diaminopyrimidine, VI., and 2-oxy-5,6-diaminopyrimidine, VII.:



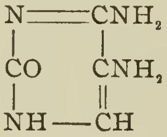
IV.



V.



VI.



VII.

Furthermore, since Kutscher obtained his base by hydrolyzing nucleic acid with sulphuric acid, at a high temperature and under pressure, it is evident that the only forms which need to be considered in the above series are those which are capable of undergoing the same treatment without complete decomposition.

Three of the pyrimidines represented above have now been synthesized: 2,4-diamino-6-oxypyrimidine, IV., has been prepared by Traube.[1] He obtained it by condensing guanidine with ethyl cyanacetate in presence of sodium ethylate. That this derivative cannot be the compound obtained by Kutscher is established by the fact that, when it is heated with 20 to 30 per cent sulphuric acid, at 130°–140°, it is completely decomposed.

Wheeler and Jamieson[2] have described 2-oxy-4,6-diaminopyrimidine, V. Their experimental evidence excludes the possibility of this pyrimidine being identical with Kutscher's base. It was easily hydrolyzed to barbituric acid when boiled with mineral acids.

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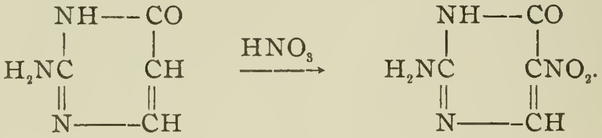
[1] Ber. d. chem. Ges., **33**, 1371.

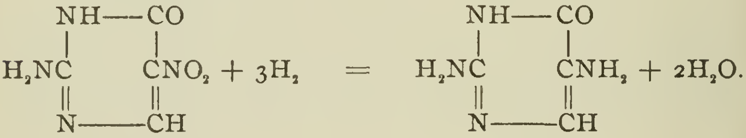
[2] THIS JOURNAL, **32**, 343 (1904).

In this paper we shall describe the preparation and properties of the diamino derivative represented by Formula VI., *viz.*: 2,5-diamino-6-oxypyrimidine. We have prepared this pyrimidine by three different methods, as follows: When isocytosine[1] was nitrated in the presence of strong sulphuric acid it was converted, practically quantitatively, into 2-amino-5-nitro-6-oxypyrimidine, VIII.:



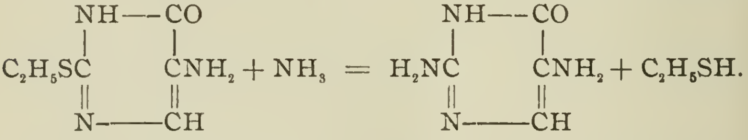
VIII.

When this nitropyrimidine was reduced in an ammoniacal solution with aluminium amalgam, it was converted, smoothly, into 2,5-diamino-6-oxypyrimidine, IX.:



IX.

The same pyrimidine was also formed when 2-ethylmercapto-5-amino-6-oxypyrimidine[2] was heated with alcoholic ammonia.



The third method which has served for the preparation of the pyrimidine was by heating bromisocytosine[3] with concentrated, aqueous ammonia.

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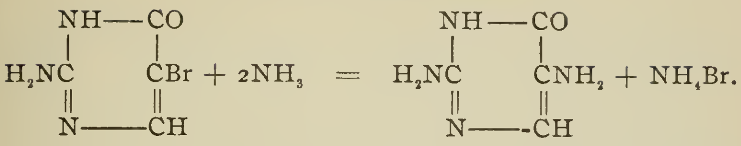
[1] Wheeler and Johnson: THIS JOURNAL, 29, 493 (1903).

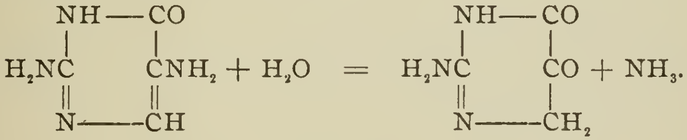
[2] Johnson: THIS JOURNAL, 34, 191 (1905).

[3] Wheeler and Johnson: *Loc. cit.*



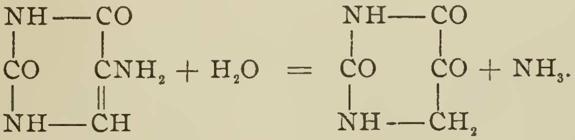
Of the three methods of preparation the first is the only one which is of practical value for the production of the base.

We now find that this 2,5-diamino-6-oxypyrimidine agrees in its chemical behavior, so far as we are able to judge, with the base which Kutscher isolated from yeast. Kutscher's meagre description of his base makes it impossible for us to establish with preciseness the identity of the two compounds. It is the first one of the above series of four pyrimidines which we have been able to heat with sulphuric acid without complete decomposition. Approximately 50 per cent of the pyrimidine was recovered unaltered, after heating with 20 per cent sulphuric acid, at 130°–140°. Part of the base was hydrolyzed by this treatment to a difficultly soluble derivative, which we have identified as 2-amino-5,6-dioxypyrimidine, X. Under the conditions employed in our work we did not observe the formation of aminouracil.



X.

This hydrolysis is perfectly analogous to the formation of oxyuracil, XI., from aminouracil, which was described by Behrend.[1]



XI.

2,5-Diamino-6-oxypyrimidine crystallizes from water with 1 molecule of water of crystallization. Analogous to Kutscher's base it gives a picrate which is extremely insoluble in water. Notwithstanding its insolubility, it is not a derivative suitable for identifying the base on account of its indefinite decomposition-point and poor crystalline form. The base also forms a beautiful crystalline series of salts with nitric, hydrochloric and sulphuric acids.

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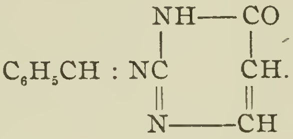
[1] Ann. Chem. (Liebig), 229, 40.

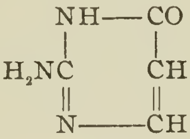
Especially interesting in connection with the nitration of isocytosine was the behavior of its benzal derivative, XII., towards nitric acid:



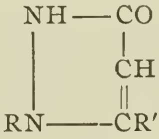
XII.

While isocytosine nitrates vary easily, to give the 2-amino-5-nitro-6-oxypyrimidine, VIII, its benzal derivative could be recovered unaltered after warming with a mixture of nitric acid (sp. gr. 1.5) and concentrated sulphuric acid, for 24 hours.

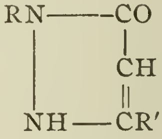
On account of their close structural relationship, it might be expected that 2-amino-6-oxypyrimidine, XIII, would show some analogy in its chemical behavior to a 3-pyrazolone, XIV., or a 5-pyrazolone, XV.:



XIII.



XIV.



XV.

Wheeler and Bristol[1] have shown that when pyrimidine derivatives, having hydrogen both in positions 4 and 5, are attacked by halogens or nitric acid, it is the hydrogen atom in position 5 which is substituted. The 3-pyrazolones[2] and 5-pyrazolones[3] are also readily attacked by halogens, the substitution taking place in position 4, which corresponds to position 5 in the pyrimidine ring. They also react smoothly, in acetic acid, with sodium nitrite to form characteristic, green-colored nitroso derivatives. We now find isocytosine does not react with nitrous acid ; it was recovered unaltered after remaining in a nitrous acid solution for several hours. We did not observe the formation of any uracil.

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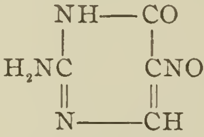
[1] This Journal, 33, 438 (1905).

[2] Ber. d. chem. Ges., 38, 154.

[3] Knorr and Duden: *Ibid.*, 25, 766.

Work on the preparation of 2-oxy-5,6-diaminopyrimidine is in progress in this laboratory.

EXPERIMENTAL.

2-Amino-5-nitro-6-oxypyrimidine, 

$$\begin{array}{ccc} \mathrm{NH} & - & \mathrm{CO} \\ | & & | \\ \mathrm{H_2NC} & & \mathrm{CNO_2} \\ \| & & \| \\ \mathrm{N} & - & \mathrm{CH} \end{array}$$

.—This nitro derivative was prepared by nitrating isocytosine.[1] After several experiments, in which we used varying proportions of nitric and sulphuric acids, we observed that we obtained the best results when we worked under the following conditions: Six grams of isocytosine were slowly added to a mixture of 18 cc. of nitric acid (sp. gr. 1.5) and 18 cc. of concentrated sulphuric acid. The nitration was very violent and, in order to avoid oxidation, the temperature of the acid mixture was not allowed to rise above 100°. After the final addition of isocytosine the mixture was heated on the steam-bath for 1 hour, to complete the reaction. Longer heating tends to diminish the yield of the nitro product. The acid mixture was thoroughly cooled and poured into 100 cc. of ice-water. The clear yellow solution that resulted was then made slightly alkaline with ammonium hydroxide. On cooling we obtained a beautiful, yellow, crystalline precipitate. It was very difficultly soluble in hot water, from which it separated, on cooling, in clusters of microscopic prisms. It was insoluble in all the ordinary organic media. It was purified for analysis by boiling with glacial acetic acid. It had no definite decomposition point, but began to turn brown at about 280° and did not decompose below 300°. The yield corresponded to 92 per cent of the theoretical. A nitrogen determination, by Kjeldahl's method, gave:

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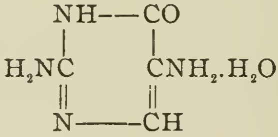
[1] Wheeler and Johnson : *Loc. cit.*

	Calculated for $C_4H_4O_3N_4$.	Found.
N	35.89	35.70

In order to establish the structure of this nitropyrimidine, it was heated with 20 per cent sulphuric acid, for 4 hours, at 190°–200°. When the solution was examined a beautiful crystalline solid had separated, which had all the properties of nitrouracil. In order to prove that this was nitrouracil it was reduced to aminouracil with aluminium amalgam, in an ammoniacal solution. That aminouracil was the product of the reduction was established by a determination of nitrogen in the free base and by means of its picrate. The picrate showed signs of decomposing at 147° and then decomposed, with violent effervescence, at 245°–247°.[1] A determination of nitrogen in the free base gave the following result:

	Calculated for $C_4H_5O_2N_3$.	Found.
N	33.07	32.99

2,5-Diamino-6-oxypyrimidine,



—Five grams of 2-amino-5-nitro-6-oxypyrimidine were suspended in 150 cc. of water, to which 5 cc. of 14 per cent ammonium hydroxide solution had been added. To this ammoniacal solution was then added an excess of aluminium amalgam and the temperature of the solution being kept below 40° during the reduction. The reduction was allowed to proceed for 24 hours, when the aluminium hydroxide was filtered off. We obtained a clear, wine-colored solution, which was concentrated on the steam-bath to about 15 cc. Decomposition took place during this evaporation and a brown, amorphous substance continued to form during prolonged heating. The concentrated solution was filtered and allowed to stand over night. In the morning 1.5 grams of crystalline material had separated. The crystals were badly etched and were developed in the form of large, radiating prisms. Associated with these prisms was a small amount of amorphous material. Some of the large prisms were removed, washed with cold water and dried in the air. The water of crystallization was determined at 120°–130°.

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[1] Wheeler and Bristol: THIS JOURNAL, 33, 438 (1905).

0.2368 gram substance lost 0.0305 gram.

	Calculated for $C_4H_6ON_4.H_2O$.	Found.
H_2O	12.50	12.88

The anhydrous base had no definite melting-point. It decomposed, with slow effervescence, at about 245°. Analysis (Kjeldahl):

	Calculated for $C_4H_6ON_4$.	Found.
N	44.44	43.96

2,5-diamino-6-oxypyrimidine is extremely soluble in water. When boiled with water the solution assumes a red color and the base apparently slowly oxidizes, with separation of a flocculent, amorphous residue. It is a strong di-acid base and forms a very characteristic series of salts (see below) with nitric, hydrochloric and sulphuric acids. Of these three salts the nitrate and hydrochloride are very soluble in water. The sulphuric acid salt is difficultly soluble in water and is the most characteristic derivative of the base that we have obtained. The base is precipitated by phosphotungstic acid and mercuric chloride. When solutions of platinum chloride and gold chloride were added to an aqueous solution of the base no double salts separated, but the halides were slowly reduced to metallic platinum and gold. With potassiobismuth iodide the base gives a brick-red precipitate.

The *picrate* was formed when picric acid was added to a dilute, aqueous solution of the base. It was very difficultly soluble in water. It separated from hot water in aggregates of short, distorted prisms (Fig. I.). Traces of impurities modify the crystal forms of the salt. Using a pure sample of the base the picrate separated in the form of stout needles. The picrate had no definite decomposition-point, but decomposed at 250°–300°, according to the rate of heating. Analysis:

	Calculated for $C_4H_6NO_4.C_6H_3O_7N_3$.	Found.
N	27.60	27.58

The *dihydrochloride*, $C_4H_6ON_4.2HCl.H_2O$, was prepared by dissolving the base in warm, concentrated hydrochloric acid. When the acid solution was allowed to stand the hydrochloride separated in magnificent, prismatic crystals, some of which measured 5 mm. in length. The prisms showed a decided tendency to twin, as shown in Fig. II. The salt contained 1 molecule of water of crystallization, which was determined by heating at 120°-130°.

0.0896 gram substance lost 0.0077 gram.

	Calculated for $C_4H_6ON_4.2HCl.H_2O$.	Found.
H_2O	8.29	8.59

Analysis of the anhydrous salt:

	Calculated for $C_4H_6ON_4.2HCl$.	Found.
N	28.14	28.07

The *nitrate*, $C_4H_6ON_4.2HNO_3$, was obtained by dissolving the base in 20 per cent nitric acid and allowing it to evaporate in a vacuum. It crystallized in beautiful prisms, which were well developed, with very distinct faces (Fig. III.). They were exceedingly soluble in water. The salt did not contain water of crystallization. Analysis:

	Calculated for $C_4H_6ON_4.2HNO_3$.	Found.
N	33.3	33.5

The *sulphate*, $C_4H_6ON_4.H_2SO_4$, was easily obtained when dilute sulphuric acid was added to an aqueous solution of the base. It was very difficultly soluble in water and separated in the form of slender, needle-like prisms. The salt showed a tendency to crystallize in two forms. When deposited from water it usually separated in clusters of radiating needles. When recrystallized from dilute sulphuric acid solution it formed beautiful, long, slender prisms with well-developed faces (Fig. IV.). Neither form contains water of crystallization. Both forms represent the same salt. The salt does not decompose below 300°.

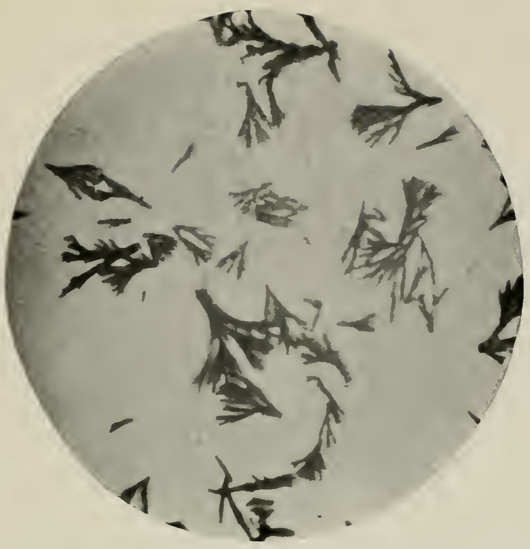

Fig. I.—The picrate of 2,5-diamino-6-oxypyrimidine crystallized from water. Magnified 60 times.

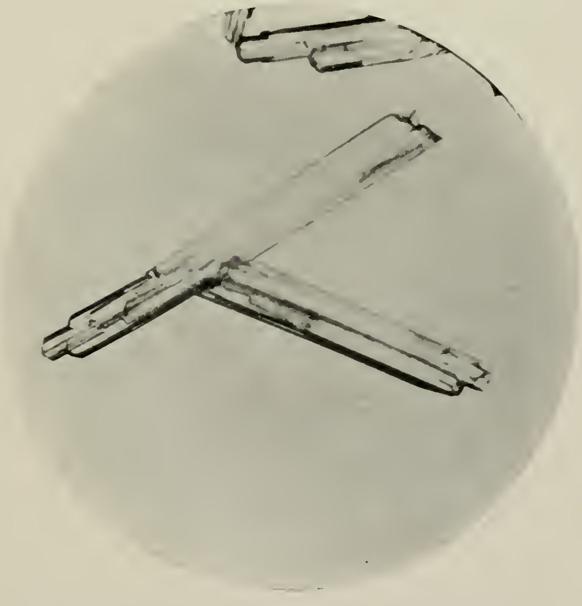

Fig II.—The hydrochloride of 2,5-diamino-6-oxypyrimidine crystallized from a strong solution of hydrochloric acid. Magnified 60 times.

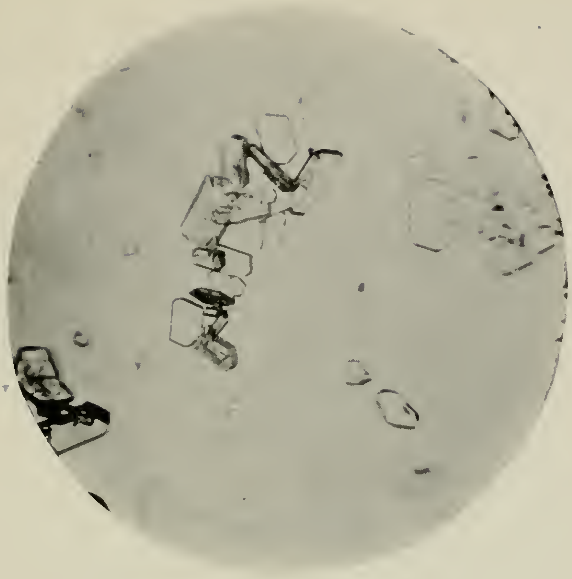

Fig. III.—The nitrate of 2,5-diamino 6-oxypyrimidine crystallized from a strong nitric acid solution. Magnified 60 times.

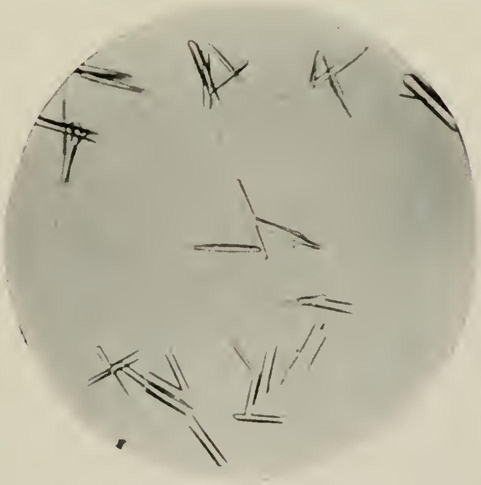

Fig. IV.—The sulphate of 2,5-diamino-6-oxypyrimidine crystallized from dilute sulphuric acid. Magnified 60 times.

Analysis of the needles and prisms of the salt :

	Calculated for $C_4H_6ON_4.H_2SO_4$.	Found. I.	II.
N	25.00	24.81	24.74

In order to avoid the possibility of dissociation in aqueous solution, solubility determinations of the sulphate were made in normal solutions of sulphuric acid. The solubility was determined by taking exactly 10 cc. of the acid solution, saturated at 25°, and determining the amount of nitrogen present (Kjeldahl). The quantity of salt dissolved in 10 cc. was then calculated from the weight of nitrogen obtained. One hundred cc. of normal sulphuric acid dissolved, at 25° :

I.	II.
0.4928 gram.	0.4704 gram.

While the 2,5-diamino-6-oxypyrimidine apparently undergoes slow decomposition when its aqueous solution is boiled, the sulphate appears to be perfectly stable when subjected to the same treatment. Some of the sulphate was dissolved in 20 per cent sulphuric acid and the solution boiled for about one-half hour. The sulphuric acid was then removed by digesting with pulverized barium carbonate. After filtering from barium carbonate and barium sulphate the filtrate was combined with a solution of picric acid. The picrate that was obtained agreed in all its properties with the picrate of 2,5-diamino-6-oxypyrimidine. Analysis :

	Calculated for $C_4H_6ON_4.C_6H_3O_7N_3$.	Found.
N	27.60	27.66

Behavior of 2,5-Diamino-6-oxypyrimidine when Heated with Sulphuric Acid under Pressure.—This experiment was of especial interest since Kutscher[1] obtained his base by hydrolyzing nucleic acid with sulphuric acid, at a high temperature and under pressure. One gram of the sulphuric acid salt of the pyrimidine base was heated in a sealed tube, with 10 cc. of sulphuric acid, of approximately 20 per cent, for 3 hours, at 130°–140°. There was no pressure when the tube was opened and no apparent decomposition had taken place. The sulphuric acid was removed by digesting with pulverized barium carbonate and, after filtering from barium carbonate and barium sulphate, the filtrate was evaporated over a free flame to about 50 cc. Some of this solution was taken and treated with a cold, saturated solution of picric acid. We obtained an immediate precipitate of a beautiful, crystalline picrate. It was extremely insoluble in water. It separated from hot water in well-developed prisms, which arranged themselves in radiating clusters. The picrate had all the properties of the picrate of 2,5-diamino-6-oxypyrimidine. Analysis (Kjeldahl):

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[1] *Loc. cit.*

	Calculated for $C_4H_6ON_4.C_6H_3O_7N_8$.	Found.
N	27.60	27.53

The remaining portion of the above filtrate, after testing for unaltered base with picric acid, was allowed to stand for 2 days, when a small amount of crystalline material separated. It was purified by recrystallizing from water, from which it separated in clusters of microscopic prisms. When heated in a capillary tube the material turned brown, but did not decompose below 300°. A nitrogen determination agreed very closely with the calculated for aminouracil or its isomer, *2-amino-5,6-dioxypyrimidine.* The low result obtained was due to the presence of a minute trace of inorganic material ($BaCO_3$?).

	Calculated for $C_4H_6O_2N_8$.	Found.
N	33.0	32.4

In order to distinguish between aminouracil and 2-amino-5,6-dioxypyrimidine, the base was dissolved in hot water and treated with a saturated solution of picric acid. The picrate separated in the form of microscopic prisms. It showed no signs of decomposing at 147°. It charred at 240°–250°, but did not effervesce below 280°. Aminouracil decomposes at 247° with violent effervescence.[1]

Action of Ammonia on Bromisocytosine or 2-Amino-5-brom-6-oxypyrimidine.—Three grams of bromisocytosine[2] were heated with an excess of aqueous ammonia, for 6 hours, at 190°–215°. When the tube was opened the solution was perfectly clear and no resin had separated. The solution gave a heavy precipitate of silver bromide when treated with nitric acid and silver nitrate. The ammoniacal solution was evaporated over a free flame to remove the excess of ammonia. On continued evaporation the solution gradually assumed a deep wine color and a slimy deposit slowly formed on the surface of the liquid. After the excess of ammonia was removed the solution was filtered and combined with a solution of picric acid, which yielded a very insoluble picrate. It was poorly crystallized and showed no definite decomposition-point. It gave no test for bromine. A nitrogen determination agreed with that calculated for the picrate of 2,5-diamino-6-oxypyrimidine.

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[1] Wheeler and Bristol: *Loc. cit.*

[2] Wheeler and Johnson: *Loc. cit.*

	Calculated for $C_4H_6NO_4.C_6H_8O_7N_8$.	Found.
N	27.60	28.10

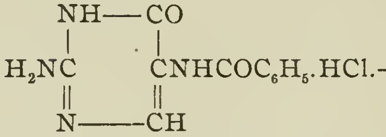
Action of Ammonia on 2-Ethylmercapto-5-amino-6-oxypyrimidine.[1]—When 2-ethylmercapto-5-amino-6-oxypyrimidine was heated in a sealed tube, with an excess of concentrated aqueous ammonia, at 131°–142°, for 4 hours it was recovered unaltered. It was again heated for 3 hours, at 180°–190°. Under these conditions only a trace of mercaptan was detected and again unaltered material was obtained. Three grams of the mercapto derivative were then heated for 4 hours, at 200°–205°, with strong alcoholic ammonia. When the tube was opened there was slight pressure and a strong odor of mercaptan. A small amount of slimy, insoluble residue had also separated. The solution was filtered and evaporated to dryness. We obtained a red-colored oil, which showed no signs of solidifying. It was dissolved in water and boiled with animal charcoal to remove the color. When the clarified solution was treated with picric acid we obtained a picrate which was difficultly soluble in water. It gave no test for sulphur and decomposed at 250°–300°, according to the rate of heating. A nitrogen determination agreed with the calculated for the picrate of 2,5-diamino-6-oxypyrimidine.

---

[1] Johnson : *Loc. cit.*

	Calculated for $C_4H_6ON_4.C_6H_3O_7N_3$.	Found.
N	27.60	27.71

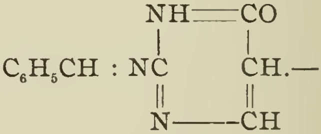
Hydrochloric Acid Salt of 2-Amino-5-benzoylamino-6-oxypyrimidine,



—An aqueous solution of guanidine was prepared by dissolving 25 grams of guanidine carbonate in water and then adding an aqueous solution containing a molecular proportion of barium hydroxide. The barium carbonate was filtered off and to the solution was added 50 grams of the sodium salt of ethyl formylhippurate. The solution was then heated on the steam-bath for 1–2 hours. The clear liquid was made distinctly acid with sulphuric acid and concentrated to about one-half its volume. Upon cooling, nothing separated. The solution was now treated with a slight excess of mercuric chloride, when a white mercury salt was obtained. This was washed with water and decomposed with hydrogen sulphide. On evaporating the filtrate, after filtering from mercuric sulphide and cooling, a crystalline product was obtained. It was insoluble in alcohol, but crystallized from hot water in microscopic needles. It contained chlorine and decomposed with violent effervescence at about 275°. We did not obtain a sufficient amount of the salt to isolate the free base. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_2N_4Cl$.	Found.
N	21.01	21.04

2-Benzalamino-6-oxypyrimidine,



—Five grams of isocytosine were heated at 160°–180°, for 3 hours, with a molecular proportion of benzaldehyde. Water was given off and a yellow, crystalline cake was obtained. It was insoluble in water and alcohol. It showed both acid and weak basic properties. It dissolved in ammonia to a deep red solution. Its salts undergo dissociation in aqueous solution. Some of the material was dissolved in 20 per cent sulphuric acid and filtered while hot into cold water. The base was precipitated at once as a yellow, crystalline solid. After washing with water and alcohol, it decomposed at 238°–242°. Analysis:

	Calculated for $C_{11}H_9ON_3$.	Found.
N	21.10	21.11

The following experiments illustrate the remarkable stability of this pyrimidine towards nitric acid: Eight and one-half grams of the crude material were dissolved in a mixture of 20 cc. of nitric acid (sp. gr. 1.5) and 15 cc. of concentrated sulphuric acid. The mixture was warmed on the steam-bath for 3 hours and then allowed to stand for 24 hours at 40°–60°. We obtained a clear, red solution. When the acid solution was poured into water a crystalline product separated which was identified as a mixture of the unaltered benzal derivative and some metanitrobenzaldehyde. After boiling with alcohol, to remove the nitrobenzaldehyde, the benzalaminopyrimidine was obtained, melting at about 242°. When mixed with the pure material the melting-point was not altered. When the benzal derivative was again heated with a mixture of nitric acid (sp. gr. 1.5) and concentrated sulphuric acid, at 90°–100°, no nitro-product was obtained but a violent oxidation took place and the pyrimidine was completely decomposed.

Action of Nitrous Acid on Isocytosine.—Four grams of isocytosine were dissolved in acetic acid. Into this solution was introduced solid sodium nitrite and the liquid allowed to stand over night, at the ordinary temperature. In the morning a crop of microscopic prisms had separated. When fused on platinum foil they left no inorganic residue. The material was very soluble in cold water. It turned brown at about 280°, but did not melt at 300°. A nitrogen determination agreed with that calculated for an acetic acid salt of isocytosine.

	Calculated for $C_6H_9O_3N_3$.	Found.
N	24.56	24.26

New Haven, Conn.,
June 7, 1905.

THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS.

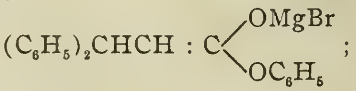
VII. COMPLEX PRODUCTS FROM CINNAMIC ESTERS.

By E. P. Kohler and Gertrude Heritage.

It has frequently been pointed out in these papers[1] that the reaction between Grignard's reagent and unsaturated esters may lead to complex products derived from 2 molecules of the unsaturated compound. As a rule, a number of these dimolecular products are formed at the same time, hence it is exceedingly difficult to isolate pure substances from the resulting mixtures. In the case of cinnamic esters, however, we have succeeded in separating a sufficient number to show the general course of the reaction.

In anticipation of experimental difficulties, we decided to begin with the phenyl ester, because phenol is easily estimated quantitatively and it is possible, therefore, to determine the amount of phenoxyl in the product. As no experiments on Grignard's reagent and phenyl esters have been described, we made a preliminary study of the action of phenylmagnesium bromide on phenyl phenylcinnamate—an ester with which no complications were to be expected. The results—published in the first part of this paper—show that phenyl esters of unsaturated acids react essentially like alkyl esters. In accordance with this we found that, when phenyl cinnamate is added to excess of carefully cooled, ethereal phenylmagnesium bromide, the two products are magnesium derivatives of phenyl diphenylpropionate and diphenylpropiophenone :

$$C_6H_5CH : CHCO_2C_6H_5 + C_6H_5MgBr \quad =$$



$$(C_6H_5)_2CHCH : C\begin{cases} OMgBr \\ OC_6H_5 \end{cases} ;$$

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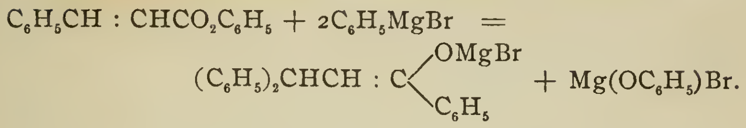
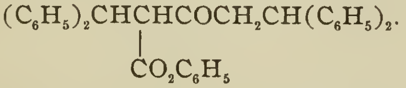
[1] This Journal, **31**, 643 ; **33**, 21, 35, 153, 333 ; **34**, 132.



$$C_6H_5CH : CHCO_2C_6H_5 + 2C_6H_5MgBr = (C_6H_5)_2CHCH : C\left\langle\begin{array}{l}OMgBr\\C_6H_5\end{array}\right. + Mg(OC_6H_5)Br.$$

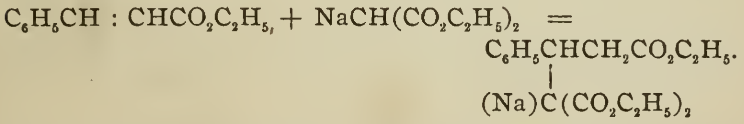
These are, therefore, the substances which subsequently form complex products by reacting with additional ester.

On reversing the procedure—adding ethereal phenylmagnesium bromide to excess of carefully cooled ester—we obtained a substance whose analysis and molecular weight correspond to the formula $C_{36}H_{30}O_3$. It will be shown, in the experimental part, that this is a β-ketonic ester, whose structure is represented by the formula



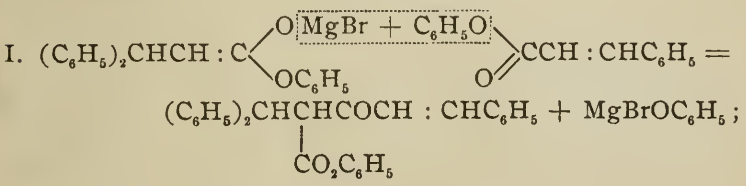
$$\begin{array}{l}(C_6H_5)_2CH\underset{\displaystyle CO_2C_6H_5}{\underset{|}{C}}HCOCH_2CH(C_6H_5)_2.\end{array}$$

It is evident, at once, that the reaction between magnesium derivatives and unsaturated esters is quite different from that which takes place between sodium derivatives and the same esters. A typical illustration of the latter is the addition of sodium malonic ester to ethyl cinnamate, which is represented by the equation

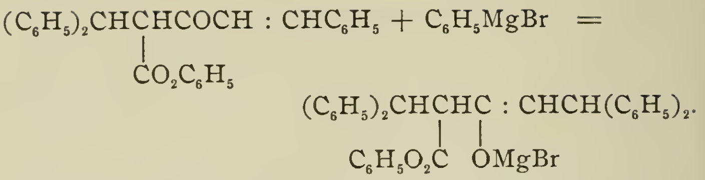


$$C_6H_5CH : CHCO_2C_2H_5 + NaCH(CO_2C_2H_5)_2 = \begin{array}{l}C_6H_5CHCH_2CO_2C_2H_5.\\\quad\;\,|\\(Na)C(CO_2C_2H_5)_2\end{array}$$

No reaction of this character could, even indirectly, lead to the ester obtained from the magnesium derivative. The most probable explanation of the latter is illustrated by the following equations:



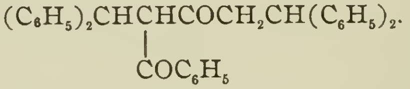
$$\text{I. } (C_6H_5)_2CHCH : C\left\langle\begin{array}{l}O\boxed{MgBr + C_6H_5O}\\OC_6H_5\qquad\qquad\quad O\end{array}\right\rangle CCH : CHC_6H_5 = (C_6H_5)_2CH\underset{\displaystyle CO_2C_6H_5}{\underset{|}{C}}HCOCH : CHC_6H_5 + MgBrOC_6H_5\,;$$

II.


$$(C_6H_5)_2CH\underset{\textstyle CO_2C_6H_5}{C}HCOCH : CHC_6H_5 + C_6H_5MgBr = (C_6H_5)_2CH\underset{\textstyle C_6H_5O_2C}{C}H\underset{\textstyle OMgBr}{C} : CHCH(C_6H_5)_2.$$

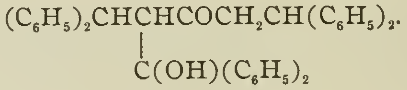
The formation of a ketol from the enolic magnesium derivative, as assumed in Equation I., is not surprising, as a corresponding rearrangement generally takes place in reactions of sodium acetoacetic ester and analogous substances. The unsaturated ketone represented as the product of the first reaction could, unfortunately, not be isolated, but we obtained considerable evidence of its formation. The magnesium derivative represented as the product of the second reaction would, on treatment with water, give the ketonic ester that was obtained.

A second dimolecular product has the composition $C_{36}H_{30}O_2$ and the structure



$$(C_6H_5)_2CH\underset{\textstyle COC_6H_5}{C}HCOCH_2CH(C_6H_5)_2.$$

This is a β-diketone, which is probably formed from the second primary product, given above, in the same way that the β-ketonic ester is formed from the first. By a subsequent reaction with phenylmagnesium bromide this ketone gives, among other substances, the magnesium derivative of a tertiary alcohol:



$$(C_6H_5)_2CH\underset{\textstyle C(OH)(C_6H_5)_2}{C}HCOCH_2CH(C_6H_5)_2.$$

EXPERIMENTAL.

I. *Experiments with Phenyl α-Phenylcinnamate.*

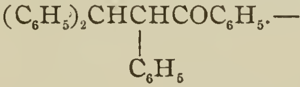
Phenyl α-phenylcinnamate was made by digesting the corresponding chloride with phenol. Both phenylcinnamic acid and its sodium salt react readily with phosphorus pentachloride. The product is a liquid that remains colorless on a steam-bath, but turns brown at higher temperatures and ultimately chars below its boiling-point, under 20 mm. pressure. The ester was, therefore, made from the crude chloride, which contained variable quantities of chlorides of phosphorus. The chloride was mixed with a considerable excess of phenol and the mixture heated on a steam-bath until there was no further evolution of hydrochloric acid. On pouring the resulting pale-yellow liquid into hot alcohol, the ester separated in stout needles These were filtered, washed thoroughly with cold alcohol and purified by recrystallization from a mixture of alcohol and chloroform.

0.2323 gram substance gave 0.7154 gram CO_2 and 0.1146 gram H_2O.

	Calculated for $C_{21}H_{16}O_2$.	Found.
C	84.00	83.99
H	5.33	5.48

The ester melts at 142°. It is very sparingly soluble in alcohol and ether, moderately in acetone and benzene, readily in chloroform.

It is interesting to note that, while methyl phenylcinnamate reacts only with 1 molecule of phenylmagnesium bromide, the corresponding phenyl ester invariably reacts with two.

Triphenylpropiophenone,  $(C_6H_5)_2CH\underset{\substack{|\\ C_6H_5}}{C}HCOC_6H_5$.—A benzene solution of phenyl phenylcinnamate was added to excess of ethereal phenylmagnesium bromide, the mixture boiled for a short time and treated in the usual way. The product was purified by solution in chloroform and precipitation with hot, absolute alcohol. It was obtained in small, colorless needles, melting at 182°. Analysis:

I. 0.1376 gram substance gave 0.4520 gram CO_2 and 0.0747 gram H_2O.

II. 0.1272 gram substance gave 0.4170 gram CO_2 and 0.0686 gram H_2O.

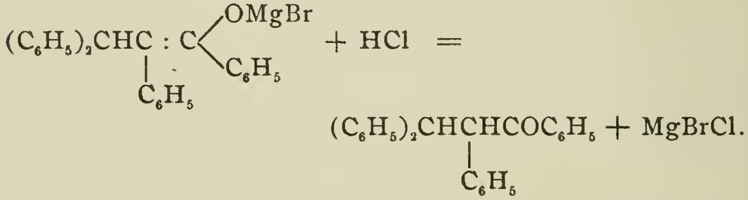
	Calculated for $C_{27}H_{22}O$.	Found. I.	II.
C	89.50	89.66	89.41
H	6.08	6.03	6.00

Molecular Weight in Boiling Acetone.

K = 1710.

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
59.6	0.691	0.055	370
"	1.415	0.120	350
"	1.954	0.161	348
		Calculated for $C_{27}H_{22}O$,	362

The ketone is readily soluble in chloroform, moderately in benzene and boiling acetone, very slightly in alcohol and ether. Like benzpinakolin, and other ketones in which the carbonyl is surrounded by a number of complex groups, it forms neither hydrazone nor oxime. A similar "steric" effect is seen in the lack of reactivity of the magnesium derivative of the ketone, for while other magnesium derivatives readily react with halogens and with acid chlorides, that of this ketone does not react with any of these substances and reacts but slowly with such as replace magnesium with hydrogen:



$$(C_6H_5)_2CH\underset{\underset{C_6H_5}{|}}{C} : C\begin{matrix} \diagup OMgBr \\ \diagdown C_6H_5 \end{matrix} + HCl =$$

$$(C_6H_5)_2CH\underset{\underset{C_6H_5}{|}}{C}HCOC_6H_5 + MgBrCl.$$

II. Phenyl Cinnamate and Phenylmagnesium Bromide.

In order to get the primary products of the reaction the substances were first brought together at the lowest temperature available. A dilute, ethereal solution of the ester (22.4 grams, 1 mol.) was added, very slowly, to an ethereal solution of phenylmagnesium bromide (3 mols.) that was cooled in a mixture of ice and ammonium chloride. The product was immediately decomposed with iced hydrochloric acid. After evaporating the ether, the residue was boiled for an hour with alcoholic potassium hydroxide. The result was 11.1 grams of diphenylpropionic acid, 12.6 grams of diphenylpropiophenone and a small quantity of diphenyl.

The experiment was repeated under exactly the same conditions, but the solution of the bromide (1 mol.) was slowly siphoned into a cooled solution of the ester (2 mol.). No solid products were obtained. The ethereal layer, on evaporation, left an oil that contained a considerable quantity of unchanged ester. This was removed by hydrolysis with alcoholic potassium hydroxide, at the ordinary temperature. After removing the potassium salts with water there remained a yellow oil which was unsaturated and which, in acetone solution, readily reduced potassium permanganate. The oxidation-products were: diphenylpropionic acid, benzoic acid and carbon dioxide. From these results we conclude that the oil consisted, mainly, of triphenylpentanone,

$$(C_6H_5)_2CHCH_2COCH : CHC_6H_5.$$

More definite results were obtained when the experiment was repeated with equimolecular amounts of the reagents. The mixture was allowed to stand over night, at the ordinary temperature and then treated in the usual way. The ethereal layer slowly deposited a crystalline solid, which was filtered, thoroughly washed with absolute alcohol and repeatedly recrystallized from a mixture of chloroform and absolute alcohol. The substance was thus obtained in long needles, melting at 180°–182°. It is readily soluble in chloroform and benzene, moderately in ethyl acetate and boiling acetone, very slightly in alcohol and ether. Analysis:

I. 0.1615 gram substance gave 0.5008 gram CO_2 and 0.0838 gram H_2O.

II. 0.1284 gram substance gave 0.3987 gram CO_2 and 0.0680 gram H_2O.

	Calculated for $C_{36}H_{30}O_3$.	Found. I.	II.
C	84.70	84.57	84.49
H	5.88	5.76	5.88

Molecular Weight in Boiling Chloroform.

$K = 39.5$.[1]

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
100.2	0.907	0.080	446
"	1.850	0.162	446
	Calculated for $C_{36}H_{30}O_3$,		510

The substance is very easily hydrolyzed. An alcoholic solution containing 4.682 grams substance was boiled, for an hour, with excess of potassium hydroxide, the alcohol distilled, the residue diluted with water and extracted with ether. The aqueous solution contained potassium phenolate and potassium carbonate, but no salt of an organic acid. It was diluted to a known volume and the phenol determined in the usual way. The result was 2.918 grams of tribromphenol, instead of 3.047 grams calculated for $C_{29}H_{25}O.CO_2C_6H_5$. The substance is, therefore, the phenol ester of a monobasic acid that loses carbon dioxide during the process of hydrolysis.

The ethereal solution, on evaporation, left 3.395 grams of a solid that was purified by recrystallization from absolute alcohol. It was deposited in colorless needles, melting at 130°. It is moderately soluble in alcohol and acetone, readily in ethyl acetate and chloroform. Analysis:

I. 0.1430 gram substance gave 0.4700 gram CO_2 and 0.0845 gram H_2O.

II. 0.1324 gram substance gave 0.4323 gram CO_2 and 0.0775 gram H_2O.

	Calculated for $C_{22}H_{26}O$.	Found. I.	Found. II.
C	89.03	89.64	89.02
H	6.66	6.56	6.44

Molecular Weight in Boiling Acetone.

$K = 1710$.

Solvent. Grams.	Substance. Grams.	Elevation of boiling-point.	Molecular weight.
52.70	0.8540	0.127	357
"	1.3975	0.226	350
	Calculated for $C_{29}H_{26}O$,		390

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[1] This value was obtained by experiment with the chloroform used.

These results show that the hydrolysis is represented by the equation

$$C_{29}H_{25}O.CO_2C_6H_5 + H_2O = C_{29}H_{26}O + C_6H_5OH + CO_2.$$

The new compound is a saturated ketone; it does not combine with bromine, it is not attacked by potassium permanganate and it forms an oxime. An alcoholic solution containing 1 molecule of the substance, 3 molecules of hydroxylamine hydrochloride and 9 molecules of potassium hydroxide was boiled for several hours, then poured into ice-water. The oxime separated as a granular solid, which was purified by crystallization from alcohol. Analysis:

I. 0.2071 gram substance gave 0.6514 gram CO_2 and 0.1274 gram H_2O.

II. 0.1905 gram substance gave 0.6113 gram CO_2 and 0.1163 gram H_2O.

	Calculated for $C_{29}H_{27}ON$.	Found.	
		I.	II.
C	85.92	85.78	86.03
H	6.66	6.83	6.69

The oxime is readily soluble in alcohol and ether, insoluble in water. From alcohol it separates in needles, melting at 115°–116°. For the purpose of rearrangement by Beckmann's reaction it was dissolved in absolute ether and treated with a slight excess of phosphorus pentachloride. The substances reacted vigorously at the ordinary temperature. The ether was removed by distillation and the horny residue boiled with water until it was completely transformed into a hard, granular solid. This was purified by repeated recrystallization from absolute alcohol. It was thus obtained in small, lustrous prisms, melting at 155°. Analysis:

0.2590 gram substance gave 0.8142 gram CO_2 and 0.1600 gram H_2O.

	Calculated for $C_{29}H_{27}ON$.	Found.
C	85.92	85.75
H	6.66	6.80

The analytical results showed that the compound is isomeric with the oxime and therefore, probably, a substituted acid anilide. This conclusion was easily verified by heating the substance with concentrated hydrochloric acid, for 8 hours, at 160°. There was no pressure on opening the tube. The contents were diluted with water and extracted with ether. The ethereal solution contained only β,β-diphenylpropionic acid, which was identified by comparison with a specimen from another source.

The aqueous solution was evaporated to complete dryness and the residue recrystallized from a small quantity of water. It separated in colorless needles, melting at 253°. This corresponds, fairly closely, to the melting-point (255°) of diphenylethylamine hydrochloride. From an aqueous solution of the salt potassium hydroxide liberated a liquid base, whose composition was determined by analysis of its platinochloride.

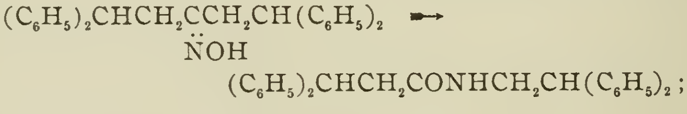
0.1495 gram salt gave 0.3685 gram Pt.

	Calculated for $C_{28}H_{32}N_2Cl_6Pt$.	Found.
Pt	24.25	24.56

These products—β,β-diphenylpropionic acid and β,β-diphenylethylamine—show that the ketone, $C_{29}H_{26}O$, is tetraphenylpentanone, the successive steps in the transformation being represented by the following equations:

$$\text{I. } [(C_6H_5)_2CHCH_2]_2CO + NH_2OH = [(C_6H_5)_2CHCH_2]_2CNOH + H_2O;$$

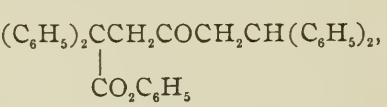
II.



$$(C_6H_5)_2CHCH_2\underset{\displaystyle \ddot{N}OH}{C}CH_2CH(C_6H_5)_2 \longrightarrow (C_6H_5)_2CHCH_2CONHCH_2CH(C_6H_5)_2;$$

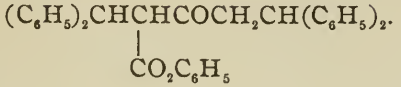
$$\text{III. } (C_6H_5)_2CHCH_2CONHCH_2CH(C_6H_5)_2 + H_2O = (C_6H_5)_2CHCH_2CO_2H + (C_6H_5)_2CHCH_2NH_2.$$

Since tetraphenylpentanone is symmetrical, there are but two possible formulas for the original product, $C_{36}H_{30}O_3$, *viz.*:



$$(C_6H_5)_2\underset{\displaystyle CO_2C_6H_5}{\underset{|}{C}}CH_2COCH_2CH(C_6H_5)_2,$$

or



$$(C_6H_5)_2CH\underset{\substack{|\\ CO_2C_6H_5}}{C}HCOCH_2CH(C_6H_5)_2.$$

The first of these formulas can be discarded at once because no substance with this structure can be formed by the interaction of phenyl cinnamate and the magnesium derivative of phenyl diphenylpropionate. The second formula represents a β-ketonic ester which, by ketone hydrolysis, should give tetraphenylpentanone, phenol and carbon dioxide and, by acid hydrolysis, 2 molecules of diphenylpropionic acid and phenol. We have shown that alcoholic potassium hydroxide gives the ketone. To determine whether acid hydrolysis is possible we heated the substance with concentrated hydrochloric acid at 180° and found that most of the product that was insoluble in water was diphenylpropionic acid—the remainder being tetraphenylpentanone. The second formula, therefore, represents the structure of the product $C_{36}H_{30}O_3$.

III. Methyl Cinnamate and Phenylmagnesium Bromide.

In an earlier paper[1] we described the result of adding the ester to excess of the magnesium compound. By reversing the procedure—adding the magnesium compound very slowly to a carefully cooled solution of the ester—we obtained a methyl ester corresponding to the phenyl ester obtained from phenyl cinnamate under the same conditions. The new compound separated as a solid when the product of the reaction was decomposed with iced hydrochloric acid. It was purified by repeated recrystallization from mixtures of chloroform and alcohol. It separated in fine needles, readily soluble in chloroform and benzene, moderately in acetone, very slightly in alcohol and ether. The melting-point is 211°–213°. Analysis:

I. 0.1910 gram substance gave 0.5820 gram CO_2 and 0.1065 gram H_2O.

II. 0.1500 gram substance gave 0.4560 gram CO_2 and 0.0851 gram H_2O.

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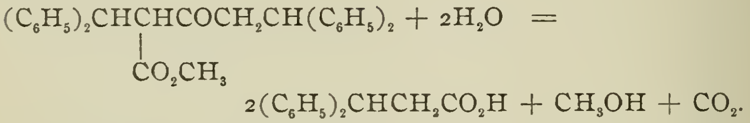
[1] This Journal, 33, 35.

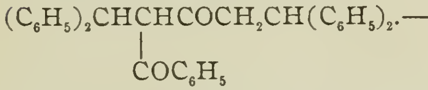
	Calculated for $C_{31}H_{28}O_3$.	Found. I.	II.
C	83.04	83.10	82.90
H	6.25	6.22	6.30

When heated to 200°, with concentrated hydrochloric acid, the substance breaks down into 2 molecules of diphenylpropionic acid :



$$(C_6H_5)_2CH\underset{\underset{\displaystyle CO_2CH_3}{|}}{C}HCOCH_2CH(C_6H_5)_2 + 2H_2O = 2(C_6H_5)_2CHCH_2CO_2H + CH_3OH + CO_2.$$

Benzoyltetraphenylpentanone,



$(C_6H_5)_2CH\underset{\underset{\displaystyle COC_6H_5}{|}}{C}HCOCH_2CH(C_6H_5)_2$.—This ketone was obtained in nearly all experiments with cinnamic esters. It separated in considerable quantity when the mother-liquor from the ester just described was diluted with alcohol and it also crystallized slowly from the oil obtained by dropping the methyl ester into a boiling solution of the magnesium compound. It was purified by recrystallization from acetone and alcohol, from which it separated in needles, melting at 166°. It is readily soluble in chloroform and acetone, moderately in alcohol, sparingly in ether. Analysis :

I. 0.1796 gram substance gave 0.5760 gram CO_2 and 0.0998 gram H_2O.

II. 0.1780 gram substance gave 0.5706 gram CO_2 and 0.0994 gram H_2O.

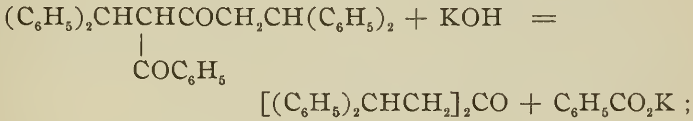
	Calculated for $C_{36}H_{30}O_2$.	Found. I.	II.
C	87.45	87.42	87.52
H	6.07	6.20	6.22

Molecular Weight Determined in Freezing Benzene.

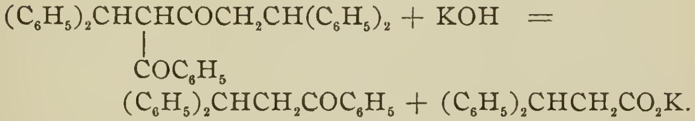
K = 50.

Solvent. Grams.	Substance. Gram.	Depression of freezing-point.	Molecular weight.
18.6080	0.4780	0.277	461
"	0.8380	0.444	470
		Calculated for $C_{36}H_{30}O_2$,	494

The structure of the ketone follows from the products of hydrolysis. Boiling alcoholic potassium hydroxide gives, mainly, tetraphenylpentanone and potassium benzoate, while boiling, concentrated, aqueous potassium hydroxide gives, mainly, diphenylpropiophenone and potassium diphenylpropionate.

I. 

$$(C_6H_5)_2CH\underset{\substack{|\\ COC_6H_5}}{C}HCOCH_2CH(C_6H_5)_2 + KOH = [(C_6H_5)_2CHCH_2]_2CO + C_6H_5CO_2K\,;$$

II. 

$$(C_6H_5)_2CH\underset{\substack{|\\ COC_6H_5}}{C}HCOCH_2CH(C_6H_5)_2 + KOH = (C_6H_5)_2CHCH_2COC_6H_5 + (C_6H_5)_2CHCH_2CO_2K.$$

Both reactions take place when the ketone is heated, at 180°, with concentrated hydrochloric acid.

A still more complex substance was obtained whenever ethereal solutions containing ester and reagent were boiled for 3 or 4 hours, before treatment with ice-water. The products, under these conditions, consist largely of oils that do not solidify, but by cautious addition of acetone and alcohol it is generally possible to get a small quantity of solid. By crystallization from chloroform this can be separated into the ketone described above and a substance which melts at 153°. It is readily soluble in acetone and chloroform, moderately in alcohol. Analysis:

I. 0.2102 gram substance gave 0.6468 gram CO_2 and 0.1129 gram H_2O.

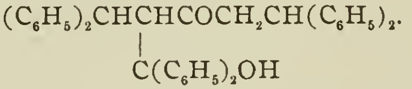
II. 0.2358 gram substance gave 0.7582 gram CO_2 and 0.1354 gram H_2O.

	Calculated for $C_{42}H_{36}O_2$.	Found.	
		I.	II.
C	88.11	87.67	87.70
H	6.28	6.23	6.37

Molecular Weight Determined in Boiling Acetone.

Solvent. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
79.68	1.1888	0.042	604
"	2.2628	0.080	605
		Calculated for $C_{42}H_{36}O$,	572

The composition and molecular weight of this compound correspond to those of the tertiary alcohol that would be obtained by the action of phenylmagnesium bromide on the ketone described above, namely :

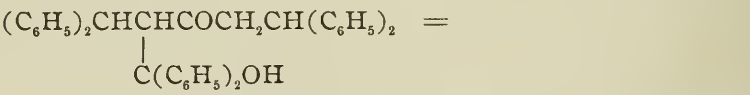


$$(C_6H_5)_2CH\underset{\substack{|\\ C(C_6H_5)_2OH}}{C}HCOCH_2CH(C_6H_5)_2.$$

The properties of the substance also agree with this formula. By the action of phenylmagnesium bromide on ethyl malonate Dilthey and Last obtained a phenacyldiphenylcarbinol whose structure is essentially like that written above. They found that when this substance was heated above its melting-point it smoothly decomposed into benzophenone and acetophenone.[1]

$$C_6H_5COCH_2C(C_6H_5)_2OH \quad = \quad C_6H_5COCH_3 + C_6H_5COC_6H_5.$$

We found that a similar change takes place when the substance under consideration is heated to 270°-300°—benzophenone distils, leaving a residue of almost pure tetraphenylpentanone :



$$(C_6H_5)_2CH\underset{\substack{|\\ C(C_6H_5)_2OH}}{C}HCOCH_2CH(C_6H_5)_2 \quad = \quad (C_6H_5)_2CHCH_2COCH_2CH(C_6H_5)_2 + (C_6H_5)_2CO.$$

The same products are obtained when the substance is heated to 200° with concentrated hydrochloric acid.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE,
June, 1905.

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[1] Ber. d. chem. Ges., **27**, 2640.

Contributions from the Chemical Laboratory of the University of Cincinnati.

LXVII.—THE USE OF POTASSIUM PERIODATE IN THE DETECTION OF MANGANESE, COBALT AND ZINC.

BY STANLEY R. BENEDICT.

Potassium periodate[1] has received few, if any, applications to qualitative analysis. There are, however, reactions obtainable with this reagent which afford very delicate, reliable and rapid methods for the detection of certain metals.

Among these is manganese. Since very satisfactory tests are already known for this element, *viz.*, formation of manganate and permanganate, the proposal of a new test for manganese would be justified only by its possession of exceptional advantages. It is believed that the test to be described possesses such advantages in the matter of time consumed and ease of manipulation, while it is by no means lacking in delicacy or in reliability.

If a solution of a manganous salt be treated with a solution of potassium periodate, a deep-red precipitate forms at once, except in very dilute solutions. In these a red coloration makes its appearance. So far as I am able to learn from literature available, this reaction between manganous salts and periodate has never been subjected to any investigation whatever. I can find no mention of the reaction nor any description of a manganese periodate in articles dealing with periodates.

I have, as yet, had time to make only a superficial examination of a few of the properties of the red precipitate obtained from manganous salts and periodate. It dissolves quite readily in hydrochloric acid, liberating some chlorine. In contact with sodium hydroxide the red precipitate changes, practically instantly, to a black substance which is, apparently, a hydrated manganese dioxide. Ammonium hydroxide produces the same change, which, in this case, goes on more slowly.

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[1] The potassium periodate referred to in this article is Kahlbaum's "potassium periodate." I have not yet determined its formula. KIO_4 is the one usually ascribed to it.

The precipitate gives the reaction for periodate which is mentioned later and, from the slight examination given it, appears to be a manganous periodate, although in color it closely resembles manganic salts, and it would seem possible that it might be a manganic iodate or periodate, a portion of the reagent serving as an oxidizing agent.

The formation of the red precipitate or coloration upon addition of periodate to a manganous solution serves as a convenient and delicate test for manganese. The reagent used is N/10 potassium periodate. The addition of 1 or 2 drops of this solution to neutral or ammoniacal solutions of manganese, produces at once a red precipitate, or, if the amount of manganese present be very small, a red coloration. If the solution be neutral the precipitate retains its color, whereas, if it be ammoniacal, the color changes quite rapidly to brown or black. The characteristic color of the manganese periodate makes its appearance in solutions as dilute as a N/10,000 manganous chloride. This is also about the limit of the red lead-nitric acid test for manganese, the depth of color obtained with the two tests being very much the same. The periodate test is slightly more delicate in neutral than in ammoniacal solutions if both solutions are cold, but in warm ammoniacal solution the test is of about equal delicacy with that in neutral solution. Warming of the ammoniacal solution is not necessary except in testing for the merest traces of manganese.

Zinc does not interfere with the periodate test for manganese. In fact periodate constitutes an excellent reagent for detecting both zinc and manganese in one solution. Pure solutions of zinc salts yield a white precipitate with periodate. If, however, ammonium chloride and ammonium hydroxide be present, this precipitation is entirely prevented in the cold unless there is a large amount of zinc, in which case a portion will be precipitated. If the solution is now filtered and the filtrate heated to boiling, the rest of the zinc is completely precipitated. The method for the detection of both elements is as follows: The sulphides are dissolved in very dilute hydrochloric acid and the solution boiled to expel hydrogen sulphide, some ammonium chloride is added and the solution made strongly ammoniacal. A few cubic centimeters of N/10 potassium periodate are now added. If a pink or red precipitate appears manganese is present. This precipitate will usually soon become brown or black in color. The solution is now filtered and a few drops of periodate added to the filtrate, to insure a slight excess of the reagent. The filtrate is then heated to boiling. Formation of a precipitate, white but colored pink by the solution if manganese was present, indicates zinc. If a white precipitate formed first upon addition of the periodate, manganese was absent and zinc present in large amount. The solution should then be filtered, a little more periodate added and the liquid heated to boiling; a white precipitate confirms zinc.

The following method for the qualitative detection and separation of manganese and zinc is proposed as requiring less periodate than does the one given above. The solution is treated with ammonium chloride and ammonium hydroxide as before. One drop of potassium periodate is added to a small portion of the solution; a pink or red coloration indicates manganese. If manganese is present, sodium phosphate is now added in slight excess to the main portion of the solution. This completely precipitates manganese, in presence of ammonium salts, without precipitating zinc. The solution is filtered and zinc detected in the filtrate by either periodate (with heating), ferrocyanide, or hydrogen sulphide.

Before leaving the subject of the reaction of manganous salts with periodate, it may be well to mention that I have frequently used manganese as a reagent for detecting periodate in presence of iodate, iodide, etc. Iodate gives neither coloration nor precipitation with manganese in presence of ammonium chloride and ammonium hydroxide, so that periodate can readily be detected, in the presence of iodate and other substances which interfere with many tests, by addition of a few drops of the solution to a solution of manganese chloride, to which has been added ammonium chloride and ammonium hydroxide. Red coloration or precipitation shows periodate. This reaction is delicate and characteristic for periodate.

In the presence of excess of nickel, the detection of cobalt is a matter of some difficulty. Vogel's[1] method, requiring the use of ammonium thiocyanate, amyl alcohol and ether, is too well known to need description here. It is probably the most delicate so far proposed and will detect 0.5 per cent of cobalt in nickel solutions. In a previous paper[2] the author described a method for the detection of both nickel and cobalt by means of sodium hydroxide solution. The method there described detects 1 per cent of cobalt in nickel solutions, the procedure being considerably simpler than in Vogel's process.

If potassium periodate be used as reagent, it is possible to detect as small an amount as 0.1 per cent of cobalt in nickel solutions. The procedure consists only in the addition of the reagent, and, if the quantity of cobalt be under 1 per cent, heating the mixture to boiling.

Addition of potassium periodate to pure nickel solutions gives a light-green precipitate, which changes only slightly upon boiling, losing some of its greenish tint and becoming faintly gray in color.

Potassium periodate added to cobalt solutions gives, at first, a dark-brown precipitate. Upon further addition of the reagent, this precipitate becomes greenish in color and finally dissolves upon heating, forming a greenish black solution.

It is upon the difference in color of the precipitates given by nickel and cobalt solutions with periodate, and the fact that the color of the cobalt precipitate makes itself apparent upon boiling, even if the amount present be very small, that the following test for cobalt depends.

To about 2–3 cc. of the solution, best N/2 to 2 N in strength, about 1 cc. of N/10 potassium periodate is added and the color of the precipitate thus obtained is observed. If it is light-green, cobalt is either entirely absent or is present in quantity under 1 per cent. The solution is now heated to boiling. If cobalt is absent the precipitate will change only very slightly, becoming somewhat lighter in color and losing some of its greenish tint. If, however, cobalt is present the precipitate will become more or less olive-green, the depth of color being dependent upon the amount of cobalt present. Where it is desired to detect very small amounts of cobalt, *i. e.*, under 0.5 per cent, it is desirable to have a check-tube containing pure nickel solution of about the same concentration as the test solution. Add periodate to both, heat to boiling and compare for one-half minute. If a greater depth of color is apparent in the test solution than in the blank, cobalt is present. If cobalt was originally present in quantity over 1 per cent, the precipitate will show a brownish- or olive-green tint in the cold, the depth of color being dependent upon the amount of cobalt present.

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[1] Ber. d. chem. Ges., **12**, 2314 (1879).

[2] J. Am. Chem. Soc., **26**, 695 (1904).

This test is very reliable and, as stated above, will detect 0.1 per cent of cobalt in nickel solutions, which is considerably less than can be detected by any other method of which I have been able to find record. Other metals than nickel and cobalt should be absent, although zinc will not interfere unless present in large amount. The solution in which the test is made should be neutral. If the precipitate turns black, either in the cold or upon boiling, manganese is present in small amount. Since this black coloration appears with the merest traces of manganese, which element is often found as impurity in nickel salts, the test becomes valuable for ascertaining the general freedom of nickel salts from manganese and cobalt.

REPORT.

Radiothorium—A New Radioactive Element.

Sir William Ramsay has recently[1] discovered a new radioactive element and has thus added another to his long list of epoch-making contributions to inorganic chemistry. This new element was found in a mineral from the island of Ceylon, called "Thorianite." Ramsay became interested in the mineral on account of the comparatively large amount of helium contained in it, 1 gram of the mineral gave off 9 cc. of helium gas.

The newly discovered element was obtained from the mineral as follows: The mineral was fused with sodium disulphate and the residue, insoluble in water, was treated with dilute, boiling hydrochloric acid. The insoluble sulphates were then fused with sodium carbonate. The barium carbonate thus obtained contained the radioactive matter in the mineral. The radium was separated by fractional crystallization of the bromides; the bromide of the new element was found to be more soluble than barium bromide.

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[1] J. Chim. Phys., 3, 617 (1905).

The new element resembles the rare earths. It forms a soluble sulphate which distinguishes it from radium. It is different from thorium in that its oxalate is insoluble in an excess of ammonium oxalate.

The new substance gives off an emanation that is identical with the thorium emanation. This is shown by its rate of decay and by the rate at which the excited activity produced by it decays.

The radioactivity of radiothorium, measured by the amount of the emanation obtainable from a given quantity of it, is *five hundred thousand times that of thorium.*

Ramsay gives the following summary of the results obtained with radiothorium: Radiothorium gives off the same emanation as thorium, but in incomparably larger quantity. The conclusion is drawn that thorium probably contains a trace of radiothorium, to which it owes its radioactivity. Ramsay has already succeeded in separating a part of the radioactivity from thorium by adding a salt of barium and then sulphuric acid. A part of the radiothorium is thus precipitated along with the barium.

Ramsay suggests the following scheme as expressing the relation between thorium, radiothorium and the helium that occurs in thorianite:

Inactive thorium → radiothorium → thorium X → emanation → thorium A → thorium B → ? → helium.

Thus, the helium found in thorianite is formed from radiothorium.

H. C. J.

REVIEWS.

Reflections Suggested by the New Theory of Matter. Being the Presidential Address before the British Association for the Advancement of Science, Cambridge, August 17, 1904. By the Right Hon. Arthur James Balfour, M.P. London, New York and Bombay: Longmans, Green & Co. 1904. pp. 24. Price, 1 Shilling net.

As would be inferred from the title, the address deals with the new views pertaining to the nature of matter, that have had their origin especially in the Cavendish laboratory. The coordination of our knowledge and the unifying effect upon physical and chemical science, resulting from the electrical conception of the nature of all matter, are pointed out.

The address is admirably written and well worthy of study on the part of all men of science, whatever their special sphere.

H. C. J.

ELETTRICITA E MATERIA. del DR. J. J. THOMSON, Professore di Fisica sperimentale nell' Università di Cambridge Membro della Societa Reale di Londra, ecc. Traduzione con Aggunte del DR. G. FAE, Libero Docente in Fisica sperimentale Professore nel R. LICEO PARINI di Milano, con 18 incisioni. Milano: Ulrico Hoepli, Editore Libraio della Real Casa. 1905. pp. 191.

Professor Thomson's Yale lectures have already been translated into German. The Italian translation has now appeared. It serves to show how widely the views of Thomson, on the relation between matter and electricity, have been accepted. The future will probably look upon these generalizations as nothing less than epoch-making in character. It is not every important advance in science that receives such wide support so quickly after it is made. H. C. J.

DIE WISSENSCHAFT. Sammlung Naturwissenschaftlicher und Mathematischer Monographien.

DIE PHYSIKALISCHEN EIGENSCHAFTEN DER SEEN. By DR. OTTO FREIHERR, von und zu AUFSESS, Assistant für Physik an der Königl. Technischen Hochschule München. Braunschweig: Druck und Verlag von Friedrich Viewig und Sohn. 1905. pp. 120. Price, M. 3.

This little book, which is illustrated by 36 diagrams, is not intended for the professional limnologist but for those who, having some slight general scientific knowledge, desire to obtain an intelligent appreciation of the physical properties of lakes and to become acquainted with the methods which are in use, at present, for the collection of the data on which this knowledge is based. After the introductory portion, pp. x + 5, the remainder of the book is divided into four parts dealing, respectively, with "mechanics," pp. 28; acoustics, pp. 3; optics, pp. 53; thermal properties, pp. 31. At the end is given a list of more special and advanced works, which will be found useful to any who desire to study the subject in greater detail. The general style of the book is clear and pleasant.

J. B. T.

NATURKONSTANTEN IN ALPHABETISCHER ANORDNUNG. Hilfsbuch für chemische und physikalische Rechnungen, mit Unterstützung des Internationalen Atomgewichtsausschusses. Herausgegeben von PROFESSOR DR. H. ERDMANN, Vorsteher des anorganisch-chemischen Laboratoriums der Königlichen Technischen Hochschule zu Berlin, und DR. P. KÖTHNER, Privatdocent in the same institution. Berlin: Verlag von Julius Springer. 1905. pp. 192 Price, M. 6.

This is a conveniently arranged table of many of the more frequently used constants, such as atomic weights, melting-points, boiling-points, densities, hardness, gas constants, electrochemical constants, critical constants, etc. The volume also contains a table of fifth-place logarithms and a comparatively large amount of valuable physical-chemical data, both thermochemical and electrochemical.

The book will be very useful in any physical or chemical laboratory. H. C. J.

OUTLINES OF INORGANIC CHEMISTRY. By FRANK AUSTIN GOOCH, Professor of Chemistry in Yale University, and CLAUDE FREDERIC WALKER, Teacher of Chemistry in the High School of Commerce of New York City. New York: Macmillan & Co. 1905. Price, $1.75 net.

In this substantial work of 516 pages the authors offer something differing in many respects from most other text-books. For this reason a review as full as the merits of the book deserve would require much space. Perhaps the briefest statement of its aims may be given by quoting the preface.

"Part I. takes up the consecutive experimental development of the principles upon which systematic chemistry rests. The consideration of identity of substances, chemical change, the chemical elements, the laws of combination and chemical equivalents naturally comes first. Electrical phenomena and ions,—the ions of Faraday—the constitution of acids, bases and salts from this ionic point of view, the conditions of action and equilibrium, and the thermal relations of chemical action are all, taken in succession, based upon the recognition of equivalents—electrical, chemical, thermal. The thermal equivalents suggest individual masses or mass-units of the elements in chemical action. Symbols are developed to express these mass-units, and the idea of valence follows. The conception of the molecule grows out of consideration of the volume occupied by the gram-equivalents of gaseous substances."

"Only in the final chapter of this part is the notion of the atom introduced, with the molecule in its relation to the atom; and here are discussed also, as matters of theory, the molecule in the light of the kinetic theory of gases, the spatial relations of van 't Hoff and of Werner, some of the phenomena of solution, the electrolytic theory of dissociation and the modern conceptions of ions."

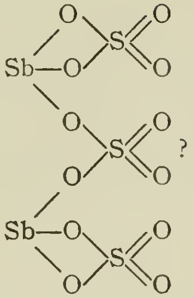
In the first part of this book the treatment of the subject is admirable. Beginning with and reasoning from simple experiments, the student is led to laws and to matters complex. Only one criticism suggests itself on this portion of the book—that some cases are too complex for students; for example, the following on valence and water of crystallization: "The attachment of water of crystallization in many salts may be attributed to the development of residual valences in the oxygen mass-unit of the water molecule. Thus we have reason to believe that the molecule of liquid water is to be regarded as a polymerized form of the molecule of gaseous water, and such polymerization may easily be represented if we are willing to assume quadrivalence of the oxygen mass-unit." Is not the quadrivalence of oxygen rather too disputed a question to present to a student, inasmuch as it is impossible to acquaint him, at this stage of study, with the experimental work and the line of reasoning on which those who favor this view base their opinion?

Another extract from the preface is: "In Part II. the discussion of the properties of elements and their compounds is taken up in accordance with a modification of Mendeléeff's Periodic System, which facilitates, as it seems to us, orderly treatment. Graphic symbols, explained as simply diagrammatic, are used freely. . . . . ."

While wishing to render justice to the generally full and always solid and scholarly treatment of the subject, objection may be made to the arrangement and to the excessive use of graphic symbols.

The Periodic System plays a curious part in the modern text-book. Some writers, like Ostwald and like Erdmann, relegate it to a couple of pages in the closing chapter, an extreme which must be deprecated. Others, like the present authors, make it the base of sequence in the discussion of the elements; this may be considered the other extreme. In Professor Gooch's own special modification of the periodic system, oxygen is the thirty-fourth element in sequence and has to wait its turn, yet this does not make so much difference after all, because the more important properties of oxygen were studied experimentally in the beginning of the first part of the book. As to Professor Gooch's modification of Mendeléeff, one can only say that he finds himself in good company, as it is at present quite the fashion for distinguished chemists to offer such modifications, witness Brauner, Werner and Abegg among the more recent. Whether any of these are—everything considered—an improvement on the original, is a debatable question.

As to graphic symbols—after they have been fully explained why continue to write them in full? No one does it in teaching organic chemistry; we should not find it necessary, in discussing the derivatives of triphenylmethane, to indicate the position and valencies of each of the carbon and hydrogen atoms in the three phenyl groups. Is it really helpful to write antimony sulphate thus,



A great deal of space is occupied by such symbols which could well have been given to other things that the authors have omitted, doubtless for lack of space. As a single example, no mention is made of the hydrides or nitrides of any of the alkali or alkaline-earth metals excepting lithium, though the importance of these hydrides to the doctrine of valence toward hydrogen in the periodic system, and the importance of calcium and magnesium nitrides, as a result of absorption of nitrogen and a source of ammonia, might have secured brief mention.

The paragraphs on processes of manufacture might be profitably enlarged or modified. Thus no mention is made of the manufacture of electrolytic sodium, or potassium, or of any manufacture or common use of sodium peroxide, or of any commercial method of making hydrochloric acid except as a by-product of the Leblanc soda process.

These are, however, comparatively trivial matters. Of the book as a whole, one can only express sincere approval and recommend it to the careful consideration of students and of chemists.

E. R.

Die Entwickelung der elektrischen Messungen. Von Dr. O. Fröhlich. Mit 124 eingedruckten Abbildungen. Braunschweig: Druck und verlag von Friedrich Vieweg und Sohn. 1905. pp. 192. Price, M. 6.

As the title implies, the book is largely of physical interest, dealing chiefly with the various forms of apparatus that have been used for electrical measurements. Considerable space is given to the historical development of the galvanometer, as we should expect. Similarly, the electrodynamometer is discussed at some length.

The various methods employed in electrical measurements are considered at the close of the volume. These include methods for measuring the current, electromotive force, resistance and self-induction.

The book will doubtless be useful to electrochemists, as well as physicists, in carrying out electrochemical measurements.

H. C. J.

THERMODYNAMIK TECHNISCHER GASREAKTIONEN. Sieben vorlesungen von DR. F. HABER, a. o., Professor an der Technischen Hochschule Karlsruhe i. B. Mit 19 Abbildungen. München and Berlin: Druck und verlag von R. Oldenbourg. 1905. pp. 296. Price, M. 10.

This book deals with a somewhat unusual subject. The idea of the ground covered can be gained best by a reference to the contents. It is published, as the title indicates, as a series of seven lectures, dealing especially with: The latent heat of chemical transformation and its relation to the energy of reaction; Entropy and its significance in gas reactions; Reactions that take place without change in the number of molecules; Reactions that take place with change in the number of molecules; Determination of the specific heat of gases; Determination of equilibrium in gases, etc.

The book represents an admirable piece of work, which is both of technical and scientific interest. Take the two chapters on gas reactions. It is difficult to say where a better account of the processes and conditions involved in these reactions can be found. The same remark applies to the chapter on the determination of the specific heat of gases. The book, as a whole, deserves high commendation. H. C. J.

LANDOLT-BÖRNSTEIN, PHYSIKALISCHE-CHEMISCHE TABELLEN. Dritte umgearbeitete und vermehrte Auflage. Herausgegeben von DR. RICHARD BÖRNSTEIN, Professor der Physik an der Landwirtschaftlichen Hochschule zu Berlin, und DR. WILHELM MEYERHOFFER, Professor, Privatdocent an der Universität zu Berlin. Berlin: Verlag von Julius Springer. 1905. pp. 861.

The character of the book in question is so well known as to call only for a brief notice. The present edition differs from the earlier in being much fuller, and especially in containing a large number of the physical-chemical constants that have recently been established.

The value of the book is greatly increased by references to the literature of the various subjects discussed. Unfortunately, however, in some instances, these are far from complete. This is notably the case in connection with the conductivity of aqueous solutions and the migration velocities of the ions.

This book is, of course, indispensable to all chemical libraries, especially in laboratories where research work is in progress. All working chemists must have access to their "Landolt-Börnstein." H. C. J.

A SYSTEMATIC COURSE OF PRACTICAL ORGANIC CHEMISTRY. By LIONEL GUY RADCLIFFE and FRANK STURDY SINNATT. London, New York and Bombay: Longmans, Green & Co. 1905. pp. 264.

The object of this book is to present a series of typical preparations which can be performed by a student working about 5 hours weekly, during one academic year. So far as can be judged from its perusal only, without using it in the laboratory, the authors have succeeded in this part of their task. They state in the preface that the course is intended "to induce the student to think, to read his theoretical text-books, to work intelligently and exactly and to recognize the connected character of the study of practical and theoretical organic chemistry." These are high aims; the first, at any rate, is hardly likely to be attained, owing to the unfortunate plan which has been adopted of stating the result of an experiment instead of leaving it to the student to observe it for himself. Thus, to mention one example out of many, in an experiment with benzoic acid, to show the action of heat, it is stated that "the acid ignites and burns with a smoky flame." Like the majority of English text-books, this one is burdened with a quantity of matter composed for the purpose of meeting the demands of certain examining boards, a blemish for which the authors are not to blame, because they explain that they are the victims of circumstances. The volume is not illustrated, the student being referred to model apparatus, which he is to copy for his own work. This plan is said to be advantageous. In spite of the drawbacks mentioned, the book, as a whole, makes a favorable impression and may be found useful to those teaching or studying the subject. J. B. T.

SPECTROSCOPY. By E. C. C. BALY, F.I.C., Lecturer on Spectroscopy and Assistant Professor of Chemistry, University College, London. (TEXT-BOOKS OF PHYSICAL CHEMISTRY. Edited by SIR WILLIAM RAMSAY, K.C.B., F.R.S.) With 163 illustrations. London, New York and Bombay: Longmans, Green & Co. 1905. pp. 568. Price, $2.80.

We all welcome another of the excellent series of physical chemistries edited by Ramsay. This latest work on spectroscopy is a fit companion of such preceding volumes as Findlay's "Phase Rule" and Mellor's "Dynamics and Statics."

The work deals with spectroscopy from the time when Sir Isaac Newton, in 1666, discovered that light of different color suffered different refraction in the same medium, up to the present.

After a historical introduction, the author takes up the prism spectroscope, discussing the separate parts—the lenses, the prism, the slit, etc., in considerable detail. The grating, and its application to spectroscopy, furnish the subject-matter for several chapters. In these the various regions of the spectra are studied at some length, including the spectra in the infra-red and in the ultra-violet.

The Zeeman effect, of course, finds its place among the newer work, and the various relations that have been pointed out between the lines produced by the same and correlated elements are developed rather fully.

The work fitly concludes with a chapter on the engine devised by Rowland for ruling the concave grating.

This book represents an admirable piece of work and is recommended to all students of the physical sciences, who must be interested in the fundamental science of spectroscopy.

H. C. J.

THE ELEMENTS OF PHYSICAL CHEMISTRY. By J. LIVINGSTON R. MORGAN, PH.D., Professor of Physical Chemistry, Columbia University. Third edition, revised and enlarged; first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. 1905. pp. xii + 510. Price, $3.00.

Attention has been called in this JOURNAL[1] to the first and second editions of this book. The following explanatory sentence occurs in the author's preface to the third edition.

"The ideas I have had in mind in making this revision may be summarized as follows: To bring the subject-matter up to date; to distinguish sharply between hypothesis and fact, avoiding the former as far as is possible; and to accentuate the physical meaning of the results of mathematical reasoning, *i. e.*, to employ mathematics simply as a means to an end and to make the matter as intelligible as possible, even to the non-mathematical reader."

H. S. U.

SELECT METHODS IN FOOD ANALYSIS. By HENRY LEFFMANN and WILLIAM BEAM. Second edition, revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1905. Price, $2.50.

The revision of this book shows the continued interest in works devoted to food analysis. The rapidly extending inspection of foods in the states and by the United States has created a demand for chemists who are experts in food analysis. The second edition of this book will prove of great advantage to chemists engaged in such work.

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[1] THIS JOURNAL, **21**, 459; **28**, 242.

The analytic methods for the determination of physical data and of chemical data are first described. Next are considered the methods of detecting poisonous metals, colors and preservatives in foods. Following this chapter are the special methods for carbohydrates, fats and oils, dairy products, non-alcoholic beverages, condiments and spices, both fermented and distilled, and alcoholic beverages. The last chapter is devoted to the examination of flesh foods and meat extracts.

The mechanical execution of the work is very commendable. The print is plain and not too small for the ordinary reader.

Among the poisonous metals which may be found in food are mentioned tin, copper, zinc and arsenic. The chapter on the detection of colors is exceptionally well written. The usual methods of detecting preservatives are described.

Many manufacturers would take exception to the statement that ale is made from a light-colored malt, usually with the addition of glucose. The occasional presence of copper, zinc, lead and arsenic in wine is ascribed to the use of crude glucose and aniline colors. In the case of copper it is more likely to be due to the spraying, which is practiced to prevent mildew and the ravages of insects. The use of shot made of lead for cleaning bottles is, perhaps, still too common, most high-grade manufacturers use shot made of tin for this purpose.

Full references are given to the most important authorities consulted. Due credit is also given to the methods employed by the Bureau of Chemistry of the Department of Agriculture and by the Association of Official Agricultural Chemists. These methods comprise a considerable portion of the whole work. The book will serve a useful purpose as a handy volume for analysts engaged in food analysis and inspection.

H. W. W.

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$C_6H_6O_2$. *p*-Diketohexamethylene. *Jackson* and *Clarke* 445

$C_6O_2Cl_4$. Tetrachlorparabenzoquinone. *Jackson* and *Clarke* 442

$C_6O_2Br_4$. Tetrabromorthobenzoquinone. *Jackson* and *Carlton* 422, 441, 442

3 VI.

$C_6HO_2Cl_3$. Trichlorparabenzoquinone. *Jackson* and *Clarke* 442

$C_6H_2O_{12}K_4$. Hydrate of. *Foote* and *Andrew* 155

$C_6H_4O_{12}Cs_2$. *Foote* and *Andrew* 156, 157, 161

C_6H_6NBr. *p*-Bromaniline. *Johnson* and *Johns*.............. 181

$C_6H_9N_3S$. 2-Ethylmercapto-6-aminopyridine. *Johnson* and *Johns*.............. 178

4 VI.

$C_6H_7N_2SCl$. 2-Ethylmercapto-6-chlorpyrimidine. *Johnson* and *Johns*.............. 177, 179

$C_6H_8N_3SCl$. 2-Ethylmercapto-4-chlor-6-aminopyrimidine. *Johnson*.............. 197

$C_6H_8N_3SBr$. 2-Ethylmercapto-5-brom-6-aminopyrimidine. *Johnson* and *Johns*.............. 178

$C_6H_9ON_3S$. 2-Ethylmercapto-5-amino-6-oxypyrimidine. *Johnson*.............. 193, 194, 199, 201, 556

$C_6H_9ON_3S$. 2-Methylmercapto-4-methoxy-6-aminopyrimidine. *Johnson* and *Johns*.............. 182

$C_6H_9ON_3S$. 2-Ethylmercapto-6-amino-4-oxypyrimidine. *Johnson* and *Johns*.............. 183

$C_6H_{11}ON_5ClS$. 2-Ethylmercapto-5-phosphoryltriamino-6-chlorpyrimidine. *Johnson*.............. 201

$C_6H_{11}ON_5S$. Phosphoryltriamide of 2-ethylmercapto-5-amino-6-oxypyrimide phosphoryldichloride. *Johnson*.............. 196

5 VI.

$C_6H_6N_2SClBr$. 2-Ethylmercapto-5-brom-6-chlorpyrimidine. *Johnson* and *Johns*.............. 177, 178, 179

$C_6H_7ON_3Cl_2S$. 2-Ethylmercapto-5-phosphoryldichloramino-6-chlorpyrimidine. *Johnson*.............. 200

6 VI.

$C_6H_7ONSPCl_2$. Phosphoryldichloride of 2-ethylmercapto-5-amino-6-oxypyrimidine. *Johnson*.............. 196

C₇-GROUP.

C_7H_6. Stilbene. *Kohler*.............. 138

$C_7H_6O_2K$. Potassium benzoate. *Kohler* and *Heritage*.............. 579

$C_7H_{11}O_4Na$. Sodium malonic ester. *Kohler* and *Heritage*.............. 569

3 VII.

$C_7H_3O_2Cl_3$. Trichlortoluquinone. *Jackson* and *Clarke*.............. 442

$C_7H_5NCl_2$. Isocyanphenyl chloride. *Wheeler* and *Statiropoulos*.............. 120

$C_7H_6Br_3N$. Tribrommonomethylaniline. *Jackson* and *Clarke*.............. 264

$C_7H_{13}O_4N$. Carbethoxyaminoethylacetate. *Johnson*.............. 192

4 VII.

$C_7H_9O_3N_3S$. 2-Ethylmercapto-5-carboxylamino-6-oxypyrimidine. *Johnson* 195, 199

5 VII.

$C_7H_7O_3N_3SAg_2$. 2-Ethylmercapto-5-carboxylamino-6-oxypyrimidine, di-silver salt of *Johnson* 200

$C_7H_8O_3NBrMg$. *Kohler* 139

C_8-GROUP.

3 VIII.

$C_8H_5O_2N$. Benzoyl isocyanate. *Wheeler* and *Statiropoulos* 121

$C_8H_6NBr_2$. Dibromdimethylaniline. *Jackson* and *Clarke* 277

$C_8H_6NBr_4$. Tribrommethylaniline hydrobromide. *Jackson* and *Clarke* 270, 287

$C_8H_9NBr_2$. Dibromdimethylaniline. *Jackson* and *Clarke* 264

$C_9H_{10}NBr_3$. Benzdibromide of bromdimethylaniline. *Jackson* and *Clarke* 267

$C_8H_{10}NBr_3$. Dibromdimethylaniline hydrobromide. *Jackson* and *Clarke* 278, 443

$C_8H_{10}NBr_5$. Benzdibromide of dimethylparabromphenylamine dibromide. *Jackson* and *Clarke* 264, 267, 269, 279

$C_8H_{10}NBr_6$. Dibromdimethylaniline tetraperbromide. *Jackson* and *Clarke* 270

$C_8H_{10}ON_2$. *p*-Nitrodimethylaniline. *Torrey* 475

$C_8H_{11}NBr_2$. Benz-3,4-dibromide of dimethylaniline. *Jackson* and *Clarke* 263, 270

$C_8H_{11}NBr_2$. Dibromdimethylaniline. *Jackson* and *Clarke* 455

$C_8H_{11}NBr_4$. Benz-3,4-dibromide of dimethylphenylamine dibromide. *Jackson* and *Clarke* 265, 266, 272, 278

$C_8H_{11}NBr_6$. Benztetrabromide of dimethylphenylamine dibromide. *Jackson* and *Clarke* 266, 279

$C_8H_{14}O_{16}N_2$. Hydrate of. *Walden* 148, 149

4 VIII.

C_8H_5ONS. Benzoyl isothiocyanate. *Wheeler* and *Statiropoulos*. 120

$C_8H_{10}NBrI_2$. *p*-Bromphenyldimethylamine diiodide. *Jackson* and *Clarke* 288, 289

$C_8H_{10}NBrI_2$. *p*-Bromphenyldimethylamine diiodide. *Jackson* and *Clarke* 268
$C_8H_{11}ON_2Br$. Nitrosodimethylaniline hydrochloride. *Torrey* 475
$C_8H_{12}O_5NNa$. Formylcarbethoxyaminoethylacetate, sodium salt of. *Johnson* 192, 197

C_9-GROUP.

C_9H_9ON. μ-Phenyloxazoline. *Johnson* 204
$C_9H_{14}NBr$. Trimethylphenylium bromide. *Jackson* and *Clarke* 443

4 IX.

$C_9H_8ON_2S$. Thiobiazolone. *Wheeler* and *Statiropoulos* 120
$C_9H_{12}ON_2S$. Ethylphenylthioncarbazinate. *Wheeler* and *Statiropoulos* 117, 119
$C_9H_{13}O_3N_3S$. 2-Ethylmercapto-5-carbethoxyamino-6-oxypyrimidine. *Johnson* 193
$C_9H_{15}O_4N_3S$. α-Carbethoxyamino-β-pseudoethylthioureaacrylic acid. *Johnson* 193
$C_9H_{15}O_4N_3S$. Trans-α-carbethoxyamino-β-pseudoethylthiourea-acrylic acid. *Johnson* 198

C_{10}-GROUP.

$C_{10}H_{12}$. Phenylbutylene. *Kohler* 147

4 X.

$C_{10}H_{10}ON_2S$. *Wheeler* and *Statiropoulos* 121
$C_{10}H_{16}NBr_3$. Benz-3,4-dibromide of dimethylethylphenylammonic bromide. *Jackson* and *Clarke* 272

C_{11}-GROUP.

$C_{11}H_{12}O_2$. Ethyl cinnamate. *Kohler* and *Heritage* 569
$C_{11}H_{12}O_2$. β-Phenylethylmalonic acid. *Kohler* 145

3 XI.

$C_{11}H_9ON_3$. 2-Benzalamino-6-oxypyrimidine. *Johnson* and *Johns* 566
$C_{11}H_9ON_3$. Benzal isocytosine. *Johnson* and *Johns* 558
$C_{11}H_{13}O_2Br$. α-Brom-β,β-methylphenylbutyric acid. *Kohler* 146
$C_{11}H_{12}N_4S$. 2-Methylmercapto-4-anilido-6-aminopyrimidine. *Johnson* and *Johns* 180, 187

4 XI.

$C_{11}H_9O_2N_3S$. 2-Thio-5-benzoylamino-6-oxypyrimidine. *Johnson* 202

$C_{11}H_{10}N_4SBr_2$. 2-Methylmercapto-4-parabromanilido-5-brom-6-aminopyrimidine. *Johnson* and *Johns* 181, 189

$C_{11}H_{10}N_4SBr_2$. 2-Methylmercapto-4-dibromanilido-6-aminopyrimidine. *Johnson* and *Johns* 181

$C_{11}H_{11}O_2N_4Cl$. Hydrochloride of 2-amino-5-benzoylamino-6-oxypyrimidine. *Johnson* and *Johns* 566

$C_{11}H_{12}O_2BrK$. Potassium bromdiphenylpropionate. *Kohler* 147

C_{12}-GROUP.

$C_{12}O_4Br_6$. Hexabromorthoquinonepyrocatechin ether. *Jackson* and *Shaffer* 461, 462, 466

$C_{12}H_{16}O_4$. Camphoroxalic acid. *Tingle* and *Hoffman* 217

$C_{12}H_{19}O_4$. *Tingle* and *Hoffman* 219

3 XII.

$C_{12}H_2O_2Cl_4$. Tetrachlorhydroquinone. *Jackson* and *Clarke* 454

$C_{12}H_{13}N_3S$. 2-Ethylmercapto-6-anilidopyrimidine. *Johnson* and *Johns* 180

$C_{12}H_{14}O_4Cu$. Copper camphoroxalate. *Tingle* and *Hoffman* 222, 238

$C_{12}H_{15}O_4Ag$. Silver camphoroxalate. *Tingle* and *Hoffman* 223, 239

$C_{12}H_{17}O_3N$. Camphoformeneaminecarboxylic acid. *Tingle* and *Hoffman* 216

$C_{12}H_{19}ON$. Methylcamphoformeneamine. *Tingle* and *Hoffman* 230, 249

C_{13}-GROUP.

$C_{13}H_{13}ON_3$. 2-Ethylmercapto-5-benzalamino-6-oxypyrimidine. *Johnson* 202

$C_{13}H_{19}O_4N_3$. Semicarbazinecamphoformeneaminecarboxylic acid *Tingle* and *Hoffman* 232, 252

$C_{13}H_{21}NO$. Dimethylcamphoformeneamine. *Tingle* and *Hoffman* 229

4 XIII.

$C_{13}H_{11}ON_3S$. 2-Ethylmercapto-5,6-(μ-phenyloxazoline) pyrimidine. *Johnson* 203, 204

$C_{13}H_{13}O_2N_3S$. *Johnson* 192

5 XIII.

$C_{13}H_{14}O_3N_3SNa$. α-Benzoylamino-β-pseudoethylthioureaacrylic acid, sodium salt. *Johnson* 192, 202

C_{14}-GROUP.

$C_{14}H_{12}$. Diphenylethylene. *Kohler* 138
$C_{14}H_{11}Cl_3$. Diphenyltrichlorethane. *Kohler* 138

3 XIV.

$C_{14}H_6O_5Br_4$. α-Ethyl alcohol tetrabromorthoquinone. *Jackson* and *Carlton* 429, 430
$C_{14}H_6O_{23}Cs_8$. *Foote* and *Andrew* 157
$C_{14}H_8O_6Br_6$. Methyl alcohol hexabromorthoquinonepyrocatechin ether. *Jackson* and *Shaffer* 463
$C_{14}H_{11}ON_3$. 1,3-Diphenyl-5-oxytriazole. *Wheeler* and *Statiropoulos* 121, 127
$C_{14}H_{11}ON_3S$. 1,4-Diphenyl-5-thiourazole. *Wheeler* and *Statiropoulos* 119
$C_{14}H_{11}O_2N_3$. 1,4-Diphenylurazole. *Wheeler* and *Statiropoulos* 118
$C_{14}H_{24}O_3N_2$. Methylamine methylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman* 230, 249

4 XIV.

$C_{14}H_{11}O_2NCl_4$. Condensation compound of chloranil and dimethylaniline. *Jackson* and *Clarke* 449
$C_{14}H_{11}O_2NBr_4$. Condensation compound of bromanil and dimethylaniline. *Jackson* and *Clarke* 451
$C_{14}H_{11}O_2NBr_4$. Condensation compound of tetrabromorthoquinone and dimethylaniline. *Jackson* and *Clarke* 448
$C_{14}H_{12}O_2NCl_3$. Condensation compound of trichlorparabenzoquinone and dimethylaniline. *Jackson* and *Clarke* 450
$C_{14}H_{13}OBrMg$. *Kohler* 141

C_{15}-GROUP.

$C_{15}H_{12}O_2$. *Kohler* 145
$C_{15}H_{16}O$. *Kohler* 145
$C_{15}H_{16}ON$. *o*-Oxybenzylidene-*p*-aminodimethylphenylamine. *Torrey* 478
$C_{15}H_{20}O_4$. Ethyl β-phenylethylmalonate. *Kohler* 145

3 XV.

$C_{15}H_8O_5Br_4$. β-Normalpropyl alcohol tetrabromorthoquinone. *Jackson* and *Carlton* 431
$C_{15}H_{12}O_2Br$. *Kohler* 138
$C_{15}H_{13}O_2Br$. α-Brom-β,β-diphenylpropionic acid. *Kohler* 139
$C_{15}H_{13}O_2K$. Potassium diphenylpropionate. *Kohler* and *Heritage* 579
$C_{15}H_{13}N_3S$. 1,3-Diphenyl-5-methylmercaptotriazole. *Wheeler* and *Statiropoulos* 131
$C_{15}H_{25}ON$. Diethyl camphoformeneamine. *Tingle* and *Hoffman* 228

4 XV.

$C_{15}H_{11}ON_3S$. α′-Benzoylimino-β′-phenylthiobiazolon. *Wheeler* and *Statiropoulos* 122, 129
$C_{15}H_{12}O_2BrK$. Potassium α-Brom-β,β-diphenylpropionate. *Kohler* 137
$C_{15}H_{13}O_2NCl_4$. Condensation compound of chloranil and dimethylparatoluidine. *Jackson* and *Clarke* 455
$C_{15}H_{14}O_2NCl_3$. Condensation compound of trichlortoluquinone and dimethylaniline. *Jackson* and *Clarke* 452
$C_{15}H_{14}O_2NCl_3$. Condensation compound of trichlorquinone and dimethylparatoluidine. *Jackson* and *Clarke* 455

C_{16}-GROUP.

$C_{16}H_{14}N_4$. 2,6-Dianilidopyrimidine. *Johnson* and *Johns* 180
$C_{16}H_{15}O_4$. Diphenylmethylmalonic acid. *Kohler* 135
$C_{16}H_{15}N_5$. 2,4-Dianilido-6-aminopyrimidine. *Johnson* and *Johns* 180, 188

3 XVI.

$C_{16}H_{15}ON_3$. 1,3-Diphenyl-5-ethoxytriazole. *Wheeler* and *Statiropoulos* 128
$C_{16}H_{15}O_2N_3$. 1,4-Diphenyl-2-ethylurazole. *Wheeler* and *Statiropoulos* 123
$C_{16}H_{15}O_2N_3$. 1,4-Diphenyl-3-ethoxyurazole. *Wheeler* and *Statiropoulos* 118, 122
$C_{16}H_{15}O_2N_3$. α-Ethoxy-α′-phenylimido-β′-phenyloxybiazoline. *Wheeler* and *Statiropoulos* 118
$C_{16}H_{22}O_4Cl_2$. Dichlordiisoamyloxyquinone. *Jackson* and *Clarke* 454
$C_{16}H_{24}O_4Cl_2$. Dichlordiisoamyloxyhydroquinone. *Jackson* and *Clarke* 454
$C_{16}H_{30}O_4N_2$. Dimethylamine dimethylcamphoformolaminecarboxylate. *Tingle* and *Hoffman* 229

4 XVI.

$C_{16}H_{15}ON_3S$. 1,4-Diphenyl-3-ethoxy-5-thiourazole. *Wheeler* and *Statiropoulos* 119, 125

$C_{16}H_{16}O_2NCl_3$. Condensation compound of bromanil and dimethylparatoluidine. *Jackson* and *Clarke* 456

$C_{16}H_{17}O_2N_3S$. Ethyl *c,b*-diphenyl-α-thionsemicarbazidate. *Wheeler* and *Statiropoulos* 117, 118

C₁₇-GROUP.

3 XVII.

$C_{17}H_{12}O_5Br_4$. α-Isoamyl alcohol tetrabromorthoquinone. *Jackson* and *Carlton* 432, 433

$C_{17}H_{17}O_2N_3$. *Wheeler* and *Statiropoulos* 121, 128

4 XVII.

$C_{17}H_{15}O_2N_3S$. α-Ethoxy-α'-benzoylimino-β'-phenylbiazoline. *Wheeler* and *Statiropoulos* 130

C₁₈-GROUP.

$C_{18}H_{18}O_4$. Monoethyl diphenylmethylmalonate. *Kohler* 135

$C_{18}H_{22}N_4$. Tetramethyldiaminoglyoxaldianil. *Torrey* 477

3 XVIII.

$C_{18}H_{10}O_4Cl_2$. Dianilinobromquinoneanil. *Jackson* and *Clarke*. 454

$C_{18}H_{17}O_2N_3$. Benzylphenylsemicarbazone. *Wheeler* and *Statiropoulos* 121

$C_{18}H_{19}ON$. *p*-Tolylcamphoformeneamine. *Tingle* and *Hoffman*. 225

$C_{18}H_{20}O_2N$. Camphoquinoxaline. *Tingle* and *Hoffman* 220

$C_{18}H_{22}O_2N_4$. *Torrey* 475

$C_{18}H_{22}O_3N$. *Tingle* and *Hoffman* 251

$C_{18}H_{22}O_3N_2$. Nitrotolylcamphoformeneamine. *Tingle* and *Hoffman* 231

$C_{18}H_{23}ON$. Benzylcamphoformeneamine. *Tingle* and *Hoffman*. 226, 245

$C_{18}H_{23}ON$. Paratolylcamphoformeneamine. *Tingle* and *Hoffman* 243

$C_{18}H_{23}O_6Na$. Addition-product of sodium malonic ester and ethyl cinnamate. *Kohler* and *Heritage* 569

$C_{18}H_{30}O_6Cl_2$. Dichlordiethoxyquinone tetraethylacetal. *Jackson* and *Clarke* 446, 454

5 XVIII.

$C_{18}H_{16}O_2NBrMg$. *Kohler* 139

C_{19}-GROUP.

3 XIX.

$C_{19}H_8O_5Br_4$. α-Benzyl alcohol tetrabromorthoquinone. *Jackson* and *Carlton*........ 427, 428

$C_{19}H_{19}O_3N$. Metatolylcamphoformeneaminecarboxylic acid. *Tingle* and *Hoffman*........ 227, 246

$C_{19}H_{19}O_3N$. *p*-Tolylcamphoformeneaminecarboxylic acid. *Tingle* and *Hoffman*........ 225, 243

$C_{19}H_{23}O_3N$. Benzylcamphoformeneaminecarboxylic acid. *Tingle* and *Hoffman*........ 226, 244

$C_{19}H_{24}O_4N_2$. *Tingle* and *Hoffman*........ 230, 250

C_{20}-GROUP.

$C_{20}H_{22}O_4$. Ethyl diphenylmethylmalonate. *Kohler*........ 134

3 XX.

$C_{20}H_{16}O_4Cl_2$. Dichlordibenzyloxyhydroquinone. *Jackson* and *Clarke*........ 455

$C_{20}H_{17}N_3S$. *Wheeler* and *Statiropoulos*........ 125

$C_{20}H_{21}O_4Br$. *Kohler*........ 137

$C_{20}H_{21}O_4Na$. *Kohler*........ 142

$C_{20}H_{24}O_2N_2$. Ethyl camphylphenylpyrazolcarboxylate. *Tingle* and *Hoffman*........ 220

$C_{20}H_{25}O_2N$. Acetyl-*p*-tolylcamphoformeneamine. *Tingle* and *Hoffman*........ 234, 253

$C_{20}H_{26}O_3N_2$. Phenylhydrazine derivative of camphoroxalic acid. *Tingle* and *Hoffman*........ 220

$C_{20}H_{33}O_4N_2$. Diethylamine diethylcamphoformolaminecarboxylate. *Tingle* and *Hoffman*........ 228, 247

4 XX.

$C_{20}H_{20}N_3SCl$. Addition compound of benzyl chloride and diphenylthiosemicarbazide. *Wheeler* and *Statiropoulos*........ 124

$C_{20}H_{21}O_4BrMg$. *Kohler*........ 132, 141

C_{21}-GROUP.

4 XXI.

$C_{21}H_{17}OBrMg$. Magnesium derivative of diphenylpropiophenone. *Kohler* and *Heritage*........ 569

$C_{21}H_{17}O_2BrMg$. Magnesium derivative of phenyl diphenylpropionate. *Kohler* and *Heritage*........ 568

$C_{21}H_{23}ON$. β-Naphthylcamphoformeneamine. *Tingle* and *Hoffman*........ 225

4 XXI.

$C_{21}H_{17}ON_3S$. 1,4-Diphenyl-3-benzylmercaptourazole. *Wheeler* and *Statiropoulos* 119, 125

C_{22}-GROUP.

$C_{22}H_{23}O_3$. β-Naphthylcamphoformeneaminecarboxylic acid. *Tingle* and *Hoffman* 225
$C_{22}H_{24}O_5$. Ethyl *o*-acetyldiphenylmethylmalonate. *Kohler* 139
$C_{22}H_{24}O_5$. *Kohler* 140, 141, 142

3 XXII.

$C_{22}H_{23}O_3N$. α-Naphthylcamphoformeneaminecarboxylic acid. *Tingle* and *Hoffman* 227
$C_{22}H_{23}O_3N$. β-Naphthylcamphoformeneaminecarboxylic acid. *Tingle* and *Hoffman* 220
$C_{22}H_{32}O_3N_2$. α-Naphthylamine α-naphthylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman* 245

C_{23}-GROUP.

$C_{23}H_{20}O$. Triphenylpentanone. *Kohler* and *Heritage* 573

4 XXIII.

$C_{23}H_{25}O_3NS$. Phenylcamphoformeneaminephenylsulphone. *Tingle* and *Hoffman* 234, 254

C_{24}-GROUP.

3 XXIV.

$C_{24}H_{22}O_8Cl_2$. Dichlordimethoxyquinone dibenzoyldimethylacetal. *Jackson* and *Clarke* 446
$C_{24}H_{26}O_3N_2$. Benzidine derivative of camphoroxalic acid. *Tingle* and *Hoffman* 231, 250
$C_{24}H_{30}O_8Ca$. Calcium camphoroxalate. *Tingle* and *Hoffman* .. 223, 240
$C_{24}H_{30}O_8Ba$. Barium camphoroxalate. *Tingle* and *Hoffman* .. 223, 239

C_{25}-GROUP.

$C_{25}H_4O_9Br_{16}$. Methyl alcohol tetrakistetrabromorthobenzoquinone. *Jackson* and *Carlton* 422
$C_{25}H_{32}O_3N_2$. Metatoluidine metatolylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman* 227

C_{26}-GROUP.

3 XXVI.

$C_{26}H_{32}O_3N_2$. Benzylamine benzylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman*.............................. 226, 244

$C_{26}H_{32}O_3N_2$. *m*-Toluidine metatolylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman*.......................... 246

$C_{26}H_{32}O_3N_2$. *p*-Toluidine *p*-tolylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman*.............................. 225, 242

C_{27}-GROUP.

$C_{27}H_{22}O$. Triphenylpropiophenone. *Kohler* and *Heritage*...... 571

C_{28}-GROUP.

$C_{28}H_{20}N_6S_2$. 1,3-Diphenyltriazole-5-disulphide. *Wheeler* and *Statiropoulos*.. 131

C_{29}-GROUP.

$C_{29}H_{26}O$. Tetraphenylpentanone. *Kohler* and *Heritage*........ 576, 579

C_{32}-GROUP.

$C_{32}H_{37}O_3$. β-Naphthylamine β-naphthylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman*...................... 224

3 XXXII.

$C_{32}H_{32}O_3N_2$. α-Naphthylamine α-naphthylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman* 226

$C_{32}H_{32}O_3N_2$. β-Naphthylamine β-naphthylcamphoformeneaminecarboxylate. *Tingle* and *Hoffman*................. 241

C_{33}-GROUP.

$C_{33}H_{32}O_4$. *Kohler*.................................. 142, 144

C_{36}-GROUP.

$C_{36}H_{30}O_2$. Benzoyl tetraphenylpentanone. *Kohler* and *Heritage* 578

$C_{36}H_{45}O_{12}Fe$. Ferric camphoroxalate. *Tingle* and *Hoffman*..... 224, 240

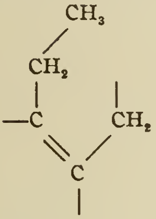
C_{42}-GROUP.

$C_{42}H_{36}O_2$. *Kohler* and *Heritage*........................... 570

ERRATA.

VOL. XXXIII.

Page.	Line.	
533		The first two formulae should be



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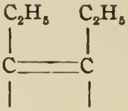

C_2H_5 C_2H_5 / $C=C$

respectively.

VOL. XXXIV.

Page.	Line.	
107	17	For inter-relas read inter-rela.
134	1	" methyl magnesium read methylmagnesium.
224	17	" β-naphthylamine-β- read β-naphthylamine β-.
227	16	" $COONH_3C_6H_4CH_3$ read $CCOONH_3C_6H_4CH_3$.
227	9[1]	" C.C read C : C.

[1] From foot.

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